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FINAL REPORT

on

MOLECULAR INTERACTIONS WITH MANY-BODY
PERTURBATION THEORY

to

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

AFOSR- 78-3661

August 31, 1981

Battelle Columbus Laboratories

Principal Investigator

Rodney J. Bartlett

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FINAL REPORT ON MOLECULAR INTERACTIONS WITH MANY-BODY PERTURBATION THEORY TO AIR
FORCE OFFICE OF SCIENTIFIC RESEARCH

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FINAL REPORT
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PERTURBATION THEORY
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AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
from
BATTELLE LABORATORIES
COLUMBUS, OHIO

I. INTRODUCTION

In a wide variety of Air Force applications, highly detailed information about atoms, molecules, and their interactions is required. (1-3)* This information is necessary in problems ranging from chemical laser development, to the detection and identification of rocket plumes, to metal clustering and aerosol formations, and even to nuclear weapons effects. (1-3)

Probably the most crucial component needed to understand molecular reactions is the potential energy surfaces that serve to describe the attractions among the atoms and molecules. (1) However, such information is not easy to obtain. A certain amount of information about the molecular forces near equilibrium in a bound molecule is available from spectroscopy. Some information about the potential energy surface even in the absence of binding can be provided from crossed molecular-beam experiments. But, in general, potential energy surfaces are not amendable to experimental determination. Instead, other types of experimental observations such as kinetics experiments, coupled with very simple

theoretical models for a surface, are used to infer pieces of information about the parameters of the model such as what the activation barrier might be.

The most direct approach to obtaining detailed information about a potential energy surface is offered by predictive, ab initio quantum mechanical calculations. However, to make it feasible to calculate accurate energy surfaces for molecules, much better and more computationally efficient methods must still be developed.

One such approach, namely many-body perturbation theory (MBPT)⁽⁴⁻¹⁵⁾ and its infinite-order extensions termed coupled-cluster methods (CCM)^(11,16-20) offer a number of attractive features that the more traditional configuration interaction approaches lack.⁽²¹⁾ Under AFOSR support at Battelle's Columbus Laboratories, very efficient computer codes to perform MBPT/CCM calculations were written and employed for the first time in large-scale ab initio calculations of potential energy surfaces.^(11,21) The successes of this effort have been substantial. These include the determination of a complete force-field for the H₂O molecule, including all force-constants through fourth-order, that is sufficiently accurate that once improved experiments were carried out after our calculations, many of the previously accepted values for the force constants were revised to be more consistent with our predictions.⁽²²⁾ Also, a study of the binding energies of the molecules B₂H₆→2BH₃, H₃BNH₃→BH₃+NH₃, and H₃BCO→BH₃+CO was made that predict these binding energies to within 1 kcal/mole of the accepted experiments for diborane and borane carbonyl, and make a prediction in the case of borazane in the absence of an experiment.⁽¹⁴⁾ Earlier experiments which gave much higher values for the binding energies of diborane and borane carbonyl than we computed are now completely discounted. Similar successes with studies of the isomerization energy and activation barrier of HNC→HCN,⁽²³⁾ and CH₃NC→CH₃CN,⁽²⁴⁾ the photo-dissociation of formaldehyde,⁽²⁵⁾ and various studies of methanol, methoxy, and the formyl radical⁽²⁶⁾ attest to the reliability of our MBPT/CCM methods.

Building upon this work supported by the AFOSR, at Battelle, we carried out extensive studies of the potential energy surface for the two inelastic collisions, $O(^3P) + H_2O$ and $O(^3P) + CO_2$, under contract to the Air Force Rocket Propulsion Laboratory, for the purpose of obtaining vibrational excitation cross-sections that are needed in actual detection devices.⁽²⁷⁾

Despite the many successes we have had, there are still categories of problems that cannot yet be attacked by MBPT/CCM. These include studies of most excited states, reactions that break multiple bonds, and applications to various kinds of open-shell molecules.⁽²¹⁾ To satisfy these additional requirements it is necessary to simultaneously develop the formal theory, write additional computer programs, and continue to make landmark applications of our developing quantum mechanical technology. Although in many cases the formal theory is less dramatic than the applications, the continual extension of the theory has a greater impact on our ability to calculate accurate energy surfaces for whatever categories of problems might emerge from the needs of the Air Force.

Consistent with this objective, much of our work has been devoted to formal theory. This includes, the derivation of the coupled-cluster single and double excitation model (CCSD)⁽²⁸⁾, optimization of orbitals within the coupled-cluster framework,⁽²⁹⁾ and developing additional mathematical techniques to efficiently solve the nonlinear coupled-cluster equations.⁽³⁰⁾ Additional applications to a variety of problems have also been accomplished.

In the following, Section II discusses the research objectives of this grant, and summarizes some of the notable accomplishments made in the past three years under our AFOSR grant at Battelle's Columbus Laboratories.

In Section III we discuss some of the research directions that work in MBPT/CCM should take in the future.

Section IV lists the publications and presentations which were supported by our three-year grant with AFOSR.

II. REVIEW OF RESEARCH ACCOMPLISHMENTS

Three years ago, when this grant was initiated, we proposed the following overall objectives:

- 1) Develop new, more accurate and more efficient ab initio quantum mechanical methods based upon MBPT and CCM for determining molecular properties, and particularly, potential energy surfaces for molecular interactions.
- 2) Implement these methods in highly efficient, transportable computer codes, to enable computations on potential energy surfaces to be made on an almost routine basis.
- 3) Apply these techniques to a variety of problems that are of interest to AFOSR, and that serve to establish the range of accuracy for MBPT and CCM methods.

In line with these objectives a number of firsts have been accomplished in this program. Highlights are reported in the annual reports of 1979 and 1980, but we will attempt to summarize some of these accomplishments together with those of the past year in this final report. The achievements in this project have been reported in 20 published papers and 30 presentations including invited lectures at most of the principal international quantum chemistry meetings. These are listed in Section IV.

Some of the principal accomplishments over the three-years of this grant include the following:

- A. The first general purpose implementation of the infinite-order coupled-cluster double excitation model (CCD) was made and applied to a number

of problems. (21,22,26) Unlike CI methods, which for practical reasons are usually restricted to single and double excitations, CCD properly includes the important effect of quadruple excitations into a molecular calculation.

- B. The first complete derivation and implementation of the coupled-cluster single and double excitation model (CCSD) has been made and initial applications recently submitted for publication. (28) The CCSD wavefunction, $e^{T_1+T_2} |\phi_0\rangle$, includes all effects of single excitations and the disconnected triple excitation terms such as $T_1 T_2$, and the quartic, T_1^4 terms. This model will be used as the framework for a new approach to chemical bonding using localized orbitals where, unlike SCF orbitals, T_1 will not necessarily be small. Since CCSD is equivalent to full CI for the chemically important problem of separated, non-interacting electron pair bonds, we expect this model to be a very interesting study in our future work.
- C. Both the infinite-order CCD and CCSD models have been extensively applied (21-27) in their truncated fourth-order form, termed DQ-MBPT(4) and SDQ-MBPT(4), when S, D, and Q refer to all single, double, and quadruple excitation MBPT diagrams that occur through fourth-order in the energy. These models have been justified by showing excellent convergence to CCD and CCSD in all cases where SCF orbitals are used and no quasi-degeneracies are encountered (21).
- D. In other work involving the theory, we have considered orbital optimization within the coupled cluster doubles model, developing a quadratically convergent scheme. (29) In future work, we intend to optimize the orbitals for the CCSD model.

E. We have studied the isomerization reactions, $\text{HNC} \rightarrow \text{HCN}$, $\text{LiNC} \rightarrow \text{LiCN}$, and $\text{BNC} \rightarrow \text{BCN}$, $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$.⁽²³⁾ Experiments exist for the first and last isomerization, while we predict the other values. In the first case, our result of 15 ± 2 kcal/mole was in disagreement with a recent experiment that obtained 10 kcal/mole.⁽³¹⁾ We published a paper claiming the experiment was in error.⁽²³⁾ Recently, W. Hehre in unpublished work has performed an ion cyclotron resonance experiment which obtains 14.8 ± 2 kcal/mole vindicating our prediction. In the case of the isomerization of methyl isocyanide our prediction of 22.7 kcal/mole is in excellent agreement with an experimental value of 23.7 obtained by Pritchard's group in Canada.⁽³²⁾

F. We have made a very thorough study of the three lowest electronic surfaces (X^1A' , a $^3A''$, and \tilde{A}^1A'') for $\text{HNO} \rightarrow \text{NO}$ this past year.⁽³³⁾ HNO is a molecule common to many flame and plume species. The emission of $\text{HNO}(A^1A'') \rightarrow \text{HNO}(X^1A')$ is responsible for the observed red emission in the reaction of $\text{H}(^2S)$ with $\text{NO}(^2\Pi)$. Geometries for all these states are obtained providing excellent agreement with experiment (within 0.02\AA and 2°) for the X^1A' and \tilde{A}^1A'' states, while predicting the structure of HNO in the a^3A'' state in the absence of experiment. Excitation energies for the two excited states and recombination rates for the $\text{H}+\text{NO} \rightarrow \text{HNO}$ reactions are also obtained.⁽³³⁾

G. The first application of CCD to a potential energy surface was our determination of the quartic force field for H_2O .⁽²²⁾ In this work we reported all force constants, made extensive comparisons with CI and with different MBPT models. Our predictions for some of the higher-order force constants differed sufficiently that Hoy and Bunker re-interpreted the infra-red data using a more flexible treatment of the

bending mode.⁽³⁴⁾ In almost every case their revised force constants were in better agreement with our prediction.

- H. Two thorough studies of the formyl radical, HCO, and its potential energy surface for the unimolecular decomposition HCO-H+CO, transition states, heats of formation, geometries, and activation barriers have been reported.⁽²⁶⁾
- I. This year, we had the opportunity to participate in a very informative comparison between MBPT/CCM and full CI. Full CI refers to including all possible n-tuple excitations within a basis set for a molecule. Because of the enormous number of configurations generated by the CI method, such a solution is impossible for anything but the simplest problems. Saxe, Schaeffer, and Handy in a notable achievement have obtained the full CI within a double-zeta basis set for H₂O.⁽³⁵⁾ This calculation used over 250,000 configurations, and required about six hours on a CDC 7600. Using our CCD model which includes double-, quadruple-, and most of the effects of higher-even ordered excitations and adding in the fourth-order single and triple excitation contributions, we obtained a result within 0.2 kcal/mole of the full CI. Our calculations, however, required only 30 seconds on a CDC 7600. Although this is an ideal system for our methods, it is an indication of the high degree of efficiency attainable by many-body methods.⁽³⁶⁾ (See review paper on MBPT/CCM written for Annual Reviews of Physical Chemistry for a discussion [36].)
- J. The structure and thermochemistry for the highly unusual pseudo tri-halogen free radical HIF has been obtained. In experiments of Yuan Lee and coworkers⁽³⁷⁾, this radical is found to be bound by 30 kcal/mole relative to IF + H, but its structure is completely unknown, without

even any evidence whether the molecule is HIF, HFI, or IHF. Also, it is not known experimentally whether or not it is linear. We have predicted its structure using MBPT/CCM and effective potentials to account for the chemically inert electrons in I. (38) The molecule is found to be bent, having a bond angle of 137° with I in the center. The IF and HI bond lengths are stretched very slightly (0.1-0.2 Å) from the corresponding bond lengths of the diatomic molecules, IF and HI. We predict a binding energy of 25 kcal/mole for decomposition to IF + H, in very good agreement with experiment.

- K. The reduced linear equation method developed for solving coupled cluster equations has been generalized by investigating a least-squares solution to the psuedo-linear CCM problem. (38)
- L. Comparisons between standard configuration interaction based methods like MCSCF, truncated CI, and full CI with MBPT/CCM methods for the insertion of Be into H_2 have been initiated. Even though this system has some very severe degeneracy problems, our initial results suggest that a single reference function CCD result can describe this insertion process adequately. The system is also serving as a vehicle to illustrate the orbital optimized CCD method.
- M. The decomposition of formaldehyde, H_2CO , to radical and molecular products and its rearrangement to hydroxycarbene has been studied. (25) This problem is of substantial experimental interest because of formaldehyde's prominence in combustion/plume processes. The activation barriers and heats of reactions have been obtained. In the latter case, agreement with experiment is within ± 2 kcal/mole. The activation barrier predictions support the CI results of Goddard and Schaeffer (39) that would suggest a tunneling mechanism for $H_2CO \rightarrow H_2 + CO$.

N. A series of detailed comparisons of various MBPT models with CCD for the C, N, and O atoms and the H_2O , NH_3 , and CH_4 molecules have been made this year.⁽²¹⁾ These comparisons, plus a number of others we have made, suggest that the infinite-order CCD results differ insignificantly from the fourth-order model, DQ-MBPT(4), for most normal cases.⁽²¹⁾ This supports the predictions of the less expensive fourth-order model for larger molecules.

O. The first all-electron ab initio coupled-cluster and MBPT calculations of benzene were made last year. This work demonstrates that a molecule of this size has at least a 20 percent error in its correlation energy due to the neglect of CI type quadruple excitations.⁽⁴⁰⁾ This emphasizes the importance of using methods like MBPT/CCM that properly include such higher order excitation effects if reliable quantum mechanical calculations are to be possible for larger molecules.

P. An investigation of the long-standing discrepancies in the experimental binding energies of the rocket fuel components, $2BH_3 \rightarrow B_2H_6$, $BH_3 + CO \rightarrow H_3BCO$, and $BH_3 + NH_3 \rightarrow H_3BNH_3$ has been made with MBPT.⁽¹⁴⁾ The binding energies of the first two are in exceptional agreement (~1 kcal/mole) with the lower set of experimental values, discounting the larger binding energies obtained from other experiments. The value of borazane of 30 kcal/mole is a prediction in the absence of any experiment.

III. FUTURE RESEARCH DIRECTIONS

Over the duration of this grant, MBPT/CCM relative to a single reference function has been shown to be a quite efficient, accurate method for ab initio calculations of molecular properties. Numerous studies of dissociation energies, molecular geometries, and force constants have attributed to this fact, as highlighted in the previous section.

MBPT/CCM relative to a single reference function is not universally applicable, however. The difficulty does not lie with MBPT/CCM but rather the limitation to a single reference function. In our work we have chosen to use an unrestricted Hartree-Fock (UHF) function to permit the description of open-shells and to correctly separate a molecule into open-shell fragments. This seems to work reliably in many open-shell cases of high multiplicity and when breaking a single bond, but the correct dissociation of multiply bonded species is more difficult to describe.

This fact is illustrated by our studies of the N_2 potential curve discussed in Appendix A. The ground state of N_2 is $^1\Sigma_g^+$, but a restricted Hartree-Fock reference function cannot separate correctly. A UHF function can, but it suffers from spin-contamination since the spin quantum number is not conserved. This is particularly bad for a singlet state, since all higher multiplicities will contaminate the lower state. Consequently, as N_2 dissociates, instead of a unit multiplicity, the multiplicity is much higher (~3.5) attributing to the high degree of contamination. This contamination causes an incorrect behavior in the UHF description of the region where N_2 starts to dissociate that subsequent correlation corrections with MBPT/CCM cannot correct. To the contrary, there are few observed problems in studying potential energy surfaces for such open-shell species as HCO , HNO , CH_3O , and $O(^3P) + H_2O$, with UHF + MBPT/CCM, since all are higher multiplicities and do not suffer

from the same degree of spin contamination.

There are potentially three solutions to the problem of dissociation of multiply bonded molecules like N_2 . The first, and simplest, would be to find a way to annihilate the spin contamination from UHF + MBPT/CCM. If a convenient prescription could be developed, this may well give a pragmatic solution of high utility.

The other two possible solutions really amount to the same thing since each introduces additional correlation corrections into the calculations, but proceed from two different directions. Either one can retain the single reference function and attempt to introduce the additional higher-order correction required to provide correct dissociations such as coupled cluster single, double, triple, etc. excitations (CCSDT...), or one could employ multiple reference functions which should not require as high an order treatment of the remainder of the corrections. The last approach is the most pervasive, but also requires the most development to obtain a theory that is convenient computationally and generally applicable. Also, the so-called quasi-degenerate forms of the multi-reference approach suffer from serious problems with intruder states, perhaps suggesting that a fixed linear combination of reference functions might be a preferable starting point.

The second approach using a single reference but a high degree of correlation has been applied by us to the very different problem of the insertion of Be into H_2 (see Appendix B). This problem has the near degeneracy of the 2s and 2p orbitals of Be as well as the degeneracy encountered when the H_2 bond is broken, where the $1\sigma_g^2$ and $1\sigma_u^2$ configurations become equally important. This system is small enough that we were able to calculate the full CI (i.e. all possible configurations) solution which is the best possible solution for the problem. The CCSD results, even relative to a single reference function

that is far from dominant in the full CI, is essentially indistinguishable from the full CI. This study emphasizes the flexibility and stability of the infinite-order coupled cluster model even when a high degree of degeneracy is present. For more complicated problems, however, perhaps multiple-reference approaches will be the only solution.

A new development which will occupy us within the future year is the consideration of particular classes of non-SCF reference functions in MBPT/CCM. SCF reference functions provide a convenient dichotomy of the energy for a molecule into the SCF part and the electron correlation effect, which is recovered by MBPT/CCM. For most problems SCF theory (at least in the unrestricted form) offers a good unperturbed approximation. Using such a function also offers a number of simplifications since all nonvanishing correlation corrections are exclusively of two-electron type. However, SCF theory has the deficiency that the canonical SCF solutions are delocalized over the entire molecule. For larger molecules, it would be useful if the orbitals were more localized since many of the two-electron integrals, $(\alpha\beta|\gamma\delta)$, would essentially vanish for charge distributions $\alpha\beta$ and $\gamma\delta$ that are adequately separated, as well as if the two orbitals in the distribution are in different regions of the molecule. The reduction in the number of nonzero integrals for a problem can have a drastic effect on the computer time required for the perturbation calculations for large molecules as well as offering a more conceptually appealing separation into units related to electron-pair bonds.

Using non-SCF reference functions raises the question how high an order in perturbation theory is required to recover the same quality of result as in SCF-based calculational methods. Also, it is necessary to add to the computer codes all the additional one-electron perturbation that using an SCF reference function eliminates. In the coming year we hope to begin to answer some of these questions.

Another area that we intend to start to investigate is the theory for the prediction of excited-state potential-energy surfaces by using equation-of-motion and related techniques built upon a MBPT/CCM ground state reference function. This is a very new direction for this project, but one that offers excellent prospects for providing excited state surfaces, which are frequently important in classes of plume and combustion problems. As a bonus, such an approach should eventually enable us to obtain electronic excitation spectra.

The fundamental idea is that for the wavefunction

$$\psi_0 = e^T |\phi_0\rangle$$

we consider a second operator, Ω , such that

$$\Omega\psi_0 = \psi_i$$

where ψ_i is some excited state. Another cluster operator is a possibility for, Ω , such as $\Omega = e^S$. From the Schrödinger equation,

$$H\psi_0 = E_0 \psi_0$$

and

$$H\psi_i = E_i \psi_i$$

$$\text{so } H\Omega\psi_0 = E_i \Omega\psi_0$$

Left multiplying the first equation by Ω , we have

$$[H, \Omega] \psi_0 = \Delta E \Omega\psi_0$$

The CC wavefunction ψ_0 may be obtained in the usual way, while a set of equations for Ω may be derived from the equation-of-motion.

In addition to the development of the theory along the lines indicated above, it is still important to pursue some applications to problems illustrating the theory at different levels with particular regard for comparisons with CI, full CI when possible, and some MCSCF results. We are interested in a variety of systems like interhalogen flame species. In particular, the unusual molecule HCF is found to be a chemiluminescence product of combustion involving combinations of interhalogen and hydrocarbon fuels, as may be important in rocket plumes. We intend to investigate the ground state energy surface for this molecule. Other categories of molecules to be studied will be largely determined by examples that are useful to illustrate the theory.

We intend to continue investigating these possibilities in our future studies at the University of Florida, Quantum Theory Project.

IV . PRESENTATIONS AND PUBLICATIONSPresentations (1981)

R. J. Bartlett, "Vibrational Excitation Cross Sections for $O(^3P) + H_2O$ and $O(^3P) + CO_2$ and Plume Detection," invited speaker, Sanibel Symposium on the Quantum Theory of Matter, March 9, 1981.

R. J. Bartlett, "Molecular Applications of Many-Body Methods," Department of Chemistry, University of Florida, Gainesville, Florida, March 16, 1981.

R. J. Bartlett, "Molecular Applications of Many-Body Methods," Department of Chemistry, Guelph University, Guelph, Ontario, Canada, March 27, 1981.

R. J. Bartlett, "Molecular Applications of Many-Body Methods," Department of Chemistry, Michigan Technological University, Houghton, Michigan, April 6, 1981.

R. J. Bartlett, "Contribution of Many-Body Methods to the Study of Energetic Materials," invited speaker, Workshop on Fundamental Research Direction for the Decomposition of Energetic Materials, Berkeley, California, January 20, 1981.

R. J. Bartlett, "Multireference Many-Body Methods for Potential Energy Surfaces," invited speaker, NRCC Sponsored meeting in Perturbation Theory, Seattle, WA, July 7, 1981.

G. D. Purvis, "Computational Implementation of the Coupled-Cluster Model," invited speaker, NRCC Sponsored meeting on Perturbation Theory, Seattle, WA, July 7, 1981.

Presentations (1980)

R. J. Bartlett, "Potential Energy Surfaces with Many-Body Methods" invited speaker, Canadian Theoretical Chemistry Conference, June 17, 1980.

R. J. Bartlett, "Many-Body Methods and Their Molecular Applications," invited speaker, New York Academy of Sciences Conference on Quantum Chemistry in the Biomedical Sciences, New York, June 2, 1980.

R. J. Bartlett, "Molecular Applications of Many-Body Perturbation Theory and Coupled Cluster Methods," Argonne National Laboratory, Argonne, IL, January, 1980.

R. J. Bartlett, "First-Principle Theoretical Predictions of Vibrational Excitation Cross-Sections for $O(^3P)$ Colliding with H_2O and CO_2 ," JANNAF Workshop on High Altitude Rocket Plumes, Colorado Springs, CO, November 19, 1980.

G. D. Purvis, "Orbital Optimization and Reduced Partitioning Method Within Coupled Cluster Theory," Sanibel Symposium on the Quantum Theory of Matter, March 13, 1980.

Presentations (1979)

R. J. Bartlett, "Molecular Applications of Coupled-Cluster and Many-Body Perturbation Methods", invited talk, Nobel Symposium on Many-Body Theory, Lerum, Sweden, June 11, 1979.

R. J. Bartlett, "Accurate Applications of Correlated Ab Initio Quantum Chemistry to Realistic Chemical Problems", Univ. of Kentucky, Lexington, Ky., February 2, 1979.

R. J. Bartlett, "Coupled-Cluster Theory for Molecular Potential Energy Surfaces", invited speaker, Sanibel Symposium on Quantum Theory of Matter, Palm Coast, Florida, March 12, 1979.

R. J. Bartlett, "Coupled Cluster Theory, Many-Body Perturbation Theory and Their Molecular Applications", Ohio University, Athens, Ohio, May 6, 1979.

R. J. Bartlett, "Have Ab Initio Quantum Mechanical Applications Finally Arrived?", University of Florida, Gainesville, Florida, May 11, 1979.

R. J. Bartlett, "Accurate Applications of Correlated Quantum Chemical Methods to Real Chemical Problems", Mount Sinai School of Medicine, New York, New York, June 4, 1979.

R. J. Bartlett, "Many-Body Perturbation Theory", Aarhus University, Aarhus, Denmark, June 18, 1979.

R. J. Bartlett, "Have Ab Initio Quantum Mechanical Applications Finally Arrived?", University of New Orleans, New Orleans, LA, October 5, 1979.

R. J. Bartlett, "Have Ab Initio Quantum Mechanical Applications Finally Arrived?", Tulane University, New Orleans, LA, October 8, 1979.

R. J. Bartlett, "Have Ab Initio Quantum Mechanical Applications Finally Arrived?", Millsaps College, Jackson, Mississippi, October 10, 1979.

R. J. Bartlett, "Have Ab Initio Quantum Mechanical Applications Finally Arrived?", University of Arkansas, Little Rock, Arkansas, October 12, 1979.

Presentations (1978)

R. J. Bartlett, "Molecular Applications of Many-Body Perturbation Theory", invited talk, American Conference on Theoretical Chemistry, Boulder, Colorado, June 29, 1978.

R. J. Bartlett, "Theoretical Contribution to the Plume Enhancement Problem", invited talk, High Altitude Infra-red Radiation Workshop, Air Force Geophysics Laboratory, Lexington, Massachusetts, August 3, 1978.

R. J. Bartlett, "Beyond Hartree-Fock: Perturbation Theory", invited talk, at the National Resource for Computation in Chemistry Workshop on "A Study of Post Hartree-Fock: Configuration Interaction", Berkeley, California, August 14, 1978.

R. J. Bartlett, "Many-Body Perturbation Theory and Coupled Cluster Methods for Molecules", Department of Applied Mathematics, University of Waterloo, Waterloo, Canada, November 13, 1978.

R. J. Bartlett, "Is Size-Consistency Important in Molecular Calculations?", Introductory Lecture, Sanibel Symposium on the Quantum Theory of Matter, Palm Coast, Florida, March, 1978.

R. J. Bartlett, "Is Size-Consistency Important in Molecular Calculations?", Midwest Theoretical Chemistry Conference, April, 1978.

G. D. Purvis, "Comparison of RHF and UHF Based Correlated Methods for the N₂ Potential Curve", Midwest Theoretical Chemistry Conference, April, 1978.

G. D. Purvis, "Comparison of RHF and UHF Based Correlation Methods for the N₂ Potential Curve", American Conference on Theoretical Chemistry, June 28, 1978.

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R. J. Bartlett, "Many-Body Perturbation Theory and Coupled Cluster Theory for Electron Correlation in Molecules," *Annual Reviews of Physical Chemistry*, Vol. 32, 359 (1981).

R. J. Bartlett and G. D. Purvis, "Electron Correlation in Large Molecules" *Annals of the New York Academy of Science*, 367, 62(1981).

G. Adams, G. Bent, R.J. Bartlett, and G.D. Purvis, III, "Formaldehyde: Electronic Structure calculations for the S_0 and T_1 States," *J.Chem.Phys.* 75,834 (1981)

G. D. Purvis, and R. J. Bartlett, "Reduced Linear Equation Method in Coupled Cluster Theory," *J. Chem. Phys.*, 75, 1284 (1981).

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APPENDIX A

MOLECULAR APPLICATIONS OF COUPLED CLUSTER AND MANY-BODY PERTURBATION
METHODS

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Rodney J. Bartlett and George D. Purvis III

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Molecular Applications of Coupled Cluster and Many-Body Perturbation Methods

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Abstract

Molecular applications of coupled cluster and many-body perturbation methods. Rodney J. Bartlett and George D. Purvis III (Battelle Columbus Laboratories, 505 King Avenue, Columbus, Ohio 43201, U.S.A.). *Physica Scripta (Sweden)* 21, 255-265, 1980.

A series of molecular applications of many-body perturbation theory (MBPT) and the coupled-cluster doubles (CCD) model are described. Even though these methods have been available for sometime, only recently have large scale, MBPT molecular calculations become available. In the case of CCD, the results presented here are among the first obtained from a general purpose *ab initio* program. The intention of this paper is to present an overview of the current state of the many-body approach to ground state properties of molecules. The properties studied are correlation energies, including contributions from single, double, and quadruple excitations diagrams in fourth- and higher-order; dissociation energies; potential energy surfaces; and molecular polarizabilities and hyperpolarizabilities. Examples are taken from studies of a variety of molecules including HF, H₂O, HCO, C₂H₆, B₂H₆, CO₂, and N₂. In many cases, it is found that quantitatively accurate dissociation energies, geometries, and force constants can be obtained. In an illustration of the X¹S_g⁻ potential energy curve of N₂, it is shown that a single UHF or RHF reference function MBPT/CCD approach is inadequate at some internuclear separation.

1. Introduction

Many-body (diagrammatic) perturbation theory (MBPT) basically dates back to Brueckner's papers [1, 2] of 1955 and Goldstone's proof of the linked-diagram theorem in 1957 [3]. Its roots include the work of Moeller and Plesset in 1934 [4], and ultimately, of course, Rayleigh-Schrödinger perturbation theory [5]. The applications to atoms originated in Kelly's work in 1963 [6], with subsequent applications by Das and co-workers [7].

Coupled cluster methods (CCM), developed by Coester and Kümmel [8, 9] in 1958-1960, and in a form useful for quantum chemistry by Čížek, Paldus, and co-workers [10-13] can be viewed as a closed-form set of equations which may be used to sum certain categories of many-body diagrams to all orders [14]. This has the advantage that order dependence is removed from the computation, and that certain invariance properties are present that would not normally apply to a finite-order method. (Within the standard MBPT framework, infinite-order summations of parts of diagrams are also frequently summed to all orders, primarily by denominator modifications, but not generally entire categories of diagrams. See, however, [15] and [16].)

The significance of MBPT/CCM and the linked-diagram theorem for chemistry has several facets. Primary among these is the concept borrowed from thermodynamics of "size-extensivity" [14]. The term indicates the proper dependence of the energy or density matrix on the size of a homogeneous

system, and is a necessary result of the exclusion of "unlinked" diagrams. A consequence of a size-extensive model is that for a group of N noninteracting H₂ molecules, $E(NH_2) = NE(H_2)$ and $\rho(NH_2) = N\rho(H_2)$. Since in a first approximation a complicated molecule can be viewed as a group of approximately noninteracting electron pair bonds like in H₂, it is apparent that the size-extensive property should be maintained as the theory is developed for larger and larger molecules. A truncated CI such as SD-CI (all single and double excitations from a reference determinant) does not have this property since it retains unlinked diagram contributions. For SD-CI $E(NH_2)$ varies as the \sqrt{N} .

Another consequence of size-extensivity for chemistry is that for a reaction consisting of closed-shell species, A + B → C + D, the heat of the reaction is given by $\Delta H_{rxn} = \Delta H_f(C) + \Delta H_f(D) - \Delta H_f(A) - \Delta H_f(B)$. This seems like an almost trivial result, however, if the heats of formation of the species were obtained by SD-CI, this simple addition is not entirely justified. In the SD-CI case, one would prefer to obtain the heat of reaction by performing "super-molecule" calculations of the two sides of the reaction with A and B and C and D infinitely far apart to partially account for the size-inextensivity. If ΔH_f is obtained by MBPT/CCM, however, a table of theoretical results for individual species may be used just as the experimental values are employed.

Although superficially similar, the correct dependence of the energy on the size of a system is a different property than correct separation of a molecule into its fragments. The latter property has sometimes been called "size-consistency" by Pople and co-workers [17, 18]. That is for any molecule AB, a method is said to be size-consistent if the predicted energies satisfy $E_{R\rightarrow\infty}(AB) = E(A) + E(B)$, where A and B may be open- or closed shell species. It is apparent that if the linked-diagram expansion is not truncated or, equivalently, if a full-CI calculation is made, then even with a single determinant reference function, size-consistency is guaranteed. The ambiguity between "size-consistency" defined as correct separation and "size-extensivity", occurs when a truncated expansion is employed, as is necessary in any practical method.

The truncation of the expansion together with the assumption of a single determinant reference function, forces a distinction between closed-shell molecules separating into closed-shell fragments and closed-shell molecules separating into open-shell fragments, due to the nature of the restricted Hartree-Fock (RHF) reference function (or any single determinant composed of doubly-occupied orbitals that reflects the point group symmetry of the molecule).

If closed-shell molecules separate into closed-shell fragments, an RHF function is a proper reference function for all inter-

nuclear separations. For this case, any approximation to the linked-diagram expansion for the energy that evaluates an *entire* diagram (i.e., not just the "diagonal" part of the diagram, for example because of possible invariance problems [26]) is size-extensive and size consistent. Hence, $E(\eta H_2) = \eta E(H_2)$, $E(\text{Mg}_2) = 2E(\text{Mg})$, and $E(\text{B}_2\text{H}_6) = 2E(\text{BH}_3)$, etc. (Note, the definition of size-consistency or correct separation only pertains to the energy, not the wavefunction where simultaneous double excitations on the various fragments are necessary even in the closed-shell case.)

However, when separation of the closed-shell molecule into open-shell fragments is required, such as in N_2 or H_2 , the RHF reference function for the molecule does not change smoothly into a single determinant RHF function for each of the fragments, but, instead, will normally go to an ionic form, A^+ and B^- . Consequently, there is no single determinant RHF reference function to employ for the open-shell fragment in a consistent MBPT/CCM calculation to investigate whether $E(\text{AB}) = E(\text{A}) + E(\text{B})$. If the level of the truncated MBPT/CCM expansion is high enough, even though the RHF reference function is separating incorrectly, the correlation corrections are sometimes sufficient to still provide a good potential curve at large intermolecular separations [32], but more frequently, it is necessary to require that the reference function should also separate correctly.

To retain the simplicity of a single determinant reference function for separation into open-shell fragments, one must normally resort to the (spin and spatially) unrestricted Hartree-Fock (UHF) type reference function. (Sometimes different possible UHF functions will converge to different separated atom limits, however, so care should be exercised.) Since the UHF function will normally converge to an RHF function for closed-shell molecules near equilibrium, the UHF function will often provide a reasonably smooth reference determinant as a function of R (see Section 5 for a contrary example), but once a bifurcation into separate RHF and UHF functions occurs, a linked-diagram expansion can be evaluated with two reference functions. By definition, both of these calculations are size-extensive since only linked-diagrams are evaluated, but only one of these two calculations would permit correct separation, or size-consistency. Hence, a single determinant reference MBPT/CCM calculation normally requires a UHF function to be both size-extensive and size-consistent, and heats of reaction with open-shell components can be computed accordingly.

A more thorough solution to the ambiguity between correct separation and the proper dependence on the size of a system, requires an open-shell MBPT/CCM approach [36-38], since a multi-determinant reference space is usually required to guarantee correct separation in a truncated expansion.

The property of size-extensivity in a theoretical model, then, is simply a consequence of a more proper treatment of quadrupole and higher CI excitations in molecular applications [14, 19, 20]. These excitations are responsible for the cancellation of unlinked diagrams. *Thus a statement that size-extensivity is important is simply a statement that quadrupole (predominantly) and higher CI excitations are important.*

These higher-excitation effects are handled in two stages in many-body methods [14, 19]. The first stage consists of incorporating higher-excitation effects to eliminate the unlinked diagrams in the theory. Thus, any approximation to the linked-diagram theorem benefits implicitly from this feature. The second stage comes where higher order CI excitations like quadrupole type $C_4(\Phi_0)$, are further decomposed into a more physi-

cally satisfying set of components, particularly $1/2 T_2^2 \Phi_0$, which represent two-simultaneous double excitations [20]. By establishing that this term out of five constitutes the predominant quadrupole excitation contribution, for closed-shell molecules, far more tractable methods for including most of the effects of quadrupole excitations are possible than within the standard CI framework [14].

In CI, multi-reference function techniques that would include all single and double excitations out of the reference determinants would introduce excitations which are four-fold relative to a single determinant, and as such, would presumably contain the most important higher excitation effects. Such a method, although not rigorously size-extensive, probably would have this property to a high-degree of accuracy.

From the foregoing, it is apparent that MBPT/CCM has much to offer in molecular problems. However, to exploit this fact in practice, it is presently necessary to use conventional finite basis sets of Slater type orbitals (STO) or contracted Gaussian type (CGTO). This is a consequence of the multicenter nature of molecular charge distributions. The few attempts to use one-center expansion techniques for molecules containing a heavy center, which permit numerical calculations as in atoms, met with very limited success [21, 22]. Hence, for more general molecular environments, basis set expansions centered at various atoms in a molecule still remain necessary. This MBPT CCM approach has been pursued by Robb [23], Bartlett and co-workers [14, 15, 19, 20, 24, 25-31], and now by several groups [17, 32-34]. The use of basis sets introduces an inherent error in the calculations, but an error that all practical quantum chemical methods share. The ultimate answer obtainable in a basis set is the "full" CI. Thus, the goal of any basis set method is to approach as closely as possible to this result. The advantages of MBPT CCM for including important effects of higher excitations suggest that MBPT/CCM has promise of converging more quickly toward the full CI result than other techniques.

In the following, we attempt to provide an overview of the current state of MBPT/CCM studies of molecular systems. Many of the results reported are new, while some particularly illuminating applications made by our group have appeared elsewhere [19, 25, 28, 29]. After a brief discussion of MBPT/CCM in Section 2, in Section 3, we study the extent of the correlation energy obtainable in a standard quality basis set and the contribution from the different orders of perturbation theory. Emphasis is placed on the importance of quadrupole excitations. In Section 4 the prediction of dissociation energies with MBPT is discussed. Section 5 describes MBPT/CCM applications to potential energy surfaces, with some comparisons with the SD-CI model. Section 6 describes MBPT applications to other properties than the energy. This includes results from the first correlated study of molecular hyperpolarizabilities [35].

2. Summary of many-body methods

A fairly complete discussion of MBPT/CCM and their relationship to CI has been given elsewhere [14]. Consequently, the present section will be limited to only a few basic equations in order to define some terms.

In MBPT the energy is given by the linked-diagram expansion [3].

$$\begin{aligned} \Delta E = E - E_0 &= E_1 + E_{\text{corr}} = \\ &= \sum_{n=0}^{\infty} \langle \Phi_0 | V[(E_0 - H_0)^{-1} V]^{n+1} | \Phi_0 \rangle_L \end{aligned} \quad (1)$$

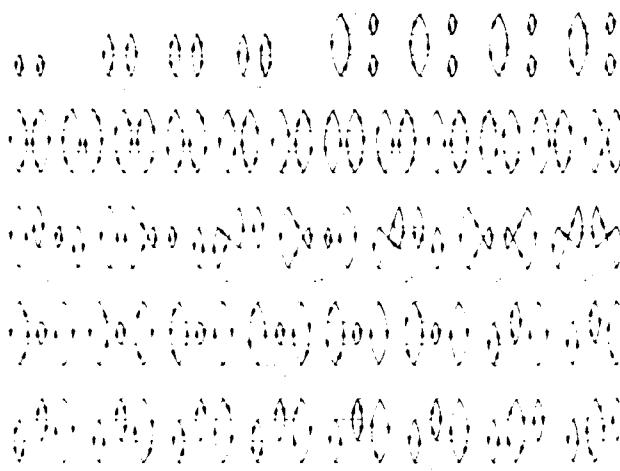


Fig. 1. Antisymmetrized Goldstone diagrams (ASGDs) through fourth order MBPT. A Hartree-Fock reference state is assumed. Orders are distinguished by the number of dashed horizontal interaction lines. Particle (ρ) and hole (h) states are represented by downward and upward directed line segments, respectively. The excitation level of a diagram is distinguished by the number of $\rho-h$ pairs intersected by an imaginary central horizontal line. In this manner the diagrams have been labeled and counted as contributions to the correlation energy arising from single (S), double (D), triple (T), and quadruple (Q) excitations types.

For the purpose of this paper, Φ_0 is the single determinant SCF result for a nondegenerate ground state.

The Hamiltonian, H_0 , is the sum of one-electron Fock operators and E_0 is the sum of the SCF orbital energies, so that $E_{\text{SCF}} = E_0 + E_1$. The perturbation is $V = H - H_0$, where H is the usual electrostatic Hamiltonian, and the subscript L indicates the limitation to linked diagrams. All the diagrams (assuming antisymmetrized vertices) that need to be considered through fourth-order are shown in Fig. 1. For purposes of discussion, these diagrams are characterized by the number of particle lines occurring in intermediate vertices into single, double, triple, and quadruple excitation types. The models are thus defined in the form SDQ-MBPT [4] which means all single, double, and quadruple excitation diagrams through fourth order in the energy. From the onset, finite basis sets are assumed, hence the SCF equations are understood to be valid in a matrix sense.

For open-shell atoms and molecules, Φ_0 is chosen to be the unrestricted Hartree-Fock (UHF)-SCF result, where relaxation of spin and spatial symmetry is permitted. The UHF solution will normally converge to the restricted (RHF) solution, which maintains spin and spatial symmetry, for ground state, closed-shell molecules, and away from the separated atom limit. For many examples RHF or UHF functions provide a reasonable starting point for a correlated method, but when this is not possible, such as when more than one determinant would be heavily weighted, it is necessary to use multireference function based methods [36-38]. In our work, the spin-multiplicity for a UHF based correlation calculation is monitored to provide evidence that the appropriate spin state is being described. Although it is better to treat open-shell problems with multireference function techniques, the greater complications involved in these methods makes the UHF approach an attractive intermediate level technique that though not of universal applicability, is of wide applicability.

The Rayleigh-Schrodinger perturbation theory (RSPT) expression for ΔE is [5].

$$\Delta E = \sum_{n=0}^{\infty} \langle \Phi_0, V[(E_0 - H_0)^{-1} P(V - \Delta E)]^n \Phi_0 \rangle \quad (2)$$

P is the projector onto the space orthogonal to Φ_0 , which, in this case, represents the space of all CI excitations from Φ_0 . Equation (2) is equal order-by-order with the linked-diagram expansion, eq. (1), if the CI excitation space is not truncated. However, if P is represented by only double-excitations from Φ_0 , then eq. (2) will converge to the D-CI solution which retains unlinked diagrams. This should be contrasted with eq. (1), where the cancellations of all unlinked-diagrams has already been achieved by permitting mixing between double and higher excitations. This cancellation is responsible for the size extensivity and the particular utility of the linked-diagram expansion.

As long as Φ_0 is the SCF result, the second- and third-order terms in eq. (2) are determined solely by CI double excitation and there is no difference between RSPT and MBPT. In the fourth order, in addition to double excitations, there are single, triple and quadruple excitations contributions. It is at this order that the difference between a truncated CI (or RSPT) and an MBPT model can occur. If P is limited to double excitations, eq. (2) gives the fourth-order approximation to D-CI, which retains unlinked, size-inextensive terms. To the contrary, the sum of the double excitation diagrams shown in Fig. 1 is a different, size-extensive approximation. On the other hand, if double and quadruple excitations are both included in P , then the fourth-order energy obtained is the same as the sum of double and quadruple excitation diagrams, or DQ-RSPT(4) = DQ-MBPT(4).

The coupled cluster method (CCM) [8-14] may be viewed as a way to sum certain categories of MBPT diagrams to all orders and this also offers a somewhat different physical insight than CI or MBPT.

For a cluster operator, \hat{T} , one considers the wavefunction [8-14, 20].

$$\psi_{\text{CC}} = e^{\hat{T}} \Phi_0 \quad (3)$$

with \hat{T} separated into one-body, two-body, etc., cluster contributions.

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots \quad (4)$$

The various parts of \hat{T} are assumed to be represented in the occupation number representation with the coefficient to be determined by the coupled-cluster equations.

For the example of CI quadruple excitations, $\hat{C}_4 \Phi_0$, from the exponential operator in eq. (3), we have the correspondence that

$$\hat{C}_4 = \hat{T}_3 + 1/2 \hat{T}_2^2 - \hat{T}_1 \hat{T}_3 + 1/2 \hat{T}_1^2 \hat{T}_2 + 1/4! \hat{T}_1^4 \quad (5)$$

This, in effect, provides a decomposition of CI quadruple excitations into five perhaps more physically meaningful components. \hat{T}_2^2 in a sense corresponds to two simultaneous interactions of two electrons, while \hat{T}_3 tends to represent a true four-body interaction [20]. Since the Hamiltonian we are considering has no more than two-body interactions, the \hat{T}_2^2 contribution would appear to be far more important than \hat{T}_3 for most closed-shell problems. This is supported by perturbation theory, where it may be shown that all fourth-order quadruple excitation contributions come from \hat{T}_2^2 , with \hat{T}_4 beginning to contribute in the fifth-order energy [14]. The remaining terms contain \hat{T}_1 which is identically zero for Brueckner orbitals, and normally found to be relatively unimportant for closed-shell systems even for SCF orbitals. As a consequence, the first reasonable coupled cluster approximation (coupled cluster doubles, CCD) has the form [10-13]

$$\Psi_{CCD} = e^{T_1} |\Phi_0\rangle \quad (6)$$

By projecting $H\Psi_{CCD}$ onto the space of double excitations, one obtains the nonlinear equations of CCD, which have the general form [13]

$$\sum_i a_{ij} t_j + \sum_{j,k} d_{ijk} t_j t_k = v_i \quad (7)$$

The coefficients a_{ij} , d_{ijk} , and v_i are simply combinations of molecular integrals while the $\{t_j\}$ are to be determined. The equations are independent of the energy which is an indication of the underlying dependence of CCD on the linked-diagram theorem. A second important consequence is that the CCD method allows one to include the predominant effect of quadruple, sextuple, etc., CI excitations within a tractable computational scheme, while in the traditional CI method, a distinction between the different components of $\hat{C}_4, \hat{C}_6, \dots$ is not possible.

In the present work, these nonlinear equations are solved iteratively. The first two iterations of the linear part of the equations provide the second-, third-, and fourth-order double excitation diagrams of Fig. 1 [14], while the first iteration of the nonlinear part of the equations (following a single linear iteration) provides the fourth-order quadruple excitation diagrams shown in Fig. 1 [14]. The remaining iterations of these equations are not easily related to an order-by-order perturbation approach. The CCD result is given as the converged solution of this procedure. (Note that many solutions of the CCD equations are, in principle, possible [39-41], but assuming normal convergence, the lowest solution should be obtained from this procedure.)

3. Correlation energies for atoms and molecules

At the present state of development of molecular theory, as contrasted with atomic theory, the use of conventional atomic

orbital basis sets centered at the various atoms or other specified locations in a molecule, remains a necessity. Some progress in numerical methods for molecules is occurring [42] but these developments are likely to be too slow to eliminate the need for basis sets for quite some time. As such, it is pertinent to develop information about what might be expected from MBPT CCM calculations with a size of basis set that can reasonably be used for a number of chemically interesting problems. The use of basis sets also means that the best possible answer is given by the "full" CI result whose agreement with experiment is a function of the calibre of the basis set.

In Tables I and II results are shown for some atoms and molecules at the level of a good but standard contracted Gaussian type orbital (CGTO) basis set. For C, N, and O the basis consists of Dunning's $5s3p$ contraction [43] of Huzinaga's primitive $9s5p$ set [44], augmented by a d -polarization function. For H, the functions consist of Dunning's $3s$ contractions with a p -polarization function. The d and p exponents are given elsewhere [29]. From Table III, it is found that this $(5s3p1d^13s1p)$ basis is capable of providing about 60-70% of the total correlation energy, and 70-80% of the valence shell correlation energy (i.e., neglecting the K -shell electrons on C, N, and O). In actual values this amounts to an error from about 0.02 Hartree up to as much as 0.20 Hartree. The error due to the basis set at the SCF level is about 0.02 Hartree for H_2O and CO, and 0.04 Hartree for CO_2 . However, in chemistry, all problems involve energy differences, and, in general, much of the basis set error will cancel to enable more reliable predictions than might be expected based upon the accuracy of the absolute energies. (See Sections 4 and 5).

The perturbation energies listed in Tables I and II all refer to the standard Moeller-Plesset (MP) splitting of the Hamiltonian with SCF (or V^N) [6] orbitals being used for the occupied and excited one-particle states. It is apparent that the second-order energy provides the predominant correlation correction. In

Table I. Energies computed by SCF(UHF), fourth-order MBPT for single, double, and quadruple diagrams, and the coupled cluster-doubles approximation. Basis sets are (531). (All energies in Hartree a.u.)

Atoms	E_{SCF}	E_1	E_2	E_3^S	E_4^D	E_4^Q	E_4^{SDQ}	DQ-MBPT(4)	CCD
C(³ P)	-37.689 13	-0.074 50	-0.015 40	-0.000 20	-0.004 67	+ 0.001 13	-0.003 74	-0.093 45	-0.094 81
(2S + 1)	3.004 2	3.002 2			3.001 9				3.001 0
N(⁴ S)	-54.398 27	-0.097 54	-0.013 96	-0.000 14	-0.002 81	+ 0.001 19	-0.001 76	-0.113 25	-0.113 19
(2S + 1)	4.002 7	4.001 6			4.001 1				4.000 7
O(³ P)	-74.806 98	-0.135 52	-0.009 65	-0.000 38	-0.002 28	-0.001 23	-0.001 43	-0.146 23	-0.149 94
(2S + 1)	3.003 9	3.002 1			3.001 5				3.000 8

^a Contribution of single excitation diagrams to (2S + 1) is not included.

Table II. Energies computed by SCF, fourth-order MBPT for single, double, and quadruple excitation diagrams, and the coupled cluster-doubles approximation. Basis sets are (531/31). (All energies in Hartree a.u.)

Molecule	E_{SCF}	E_1	E_2	E_3^S	E_4^D	E_4^Q	E_4^{SDQ}	DQ-MBPT(4)	CCD
H_2O^a	-76.047 84	-0.241 11	-0.003 69	-0.001 48	-0.003 88	+ 0.002 16	-0.003 19	-0.246 51	-0.246 66
NH_3^b	-56.209 34	-0.220 10	-0.011 61	-0.001 19	-0.004 25	+ 0.002 35	-0.002 59	-0.233 11	-0.233 40
CH_4^c	-40.206 59	-0.189 80	-0.019 69	-0.000 97	-0.004 89	+ 0.002 94	-0.002 92	-0.211 43	-0.211 ??
CO_2^d	-187.685 91	-0.520 01	+ 0.020 53	-0.011 77	-0.013 36	+ 0.008 86	-0.016 27	-0.503 98	-0.504 01
CO^e	-112.767 33	-0.309 82	+ 0.004 92	-0.006 92	-0.009 98	+ 0.004 90	-0.012 00	-0.309 97	-0.309 69

^a ($R_{OH} = 1.808b$, $\theta = 102.4^\circ$). All electrons correlated.

^b ($R_{NH} = 1.92b$, $\theta = 107.3^\circ$). All electrons correlated.

^c ($R_{CH} = 2.065b$, $\theta = 104.28^\circ$). All electrons correlated.

^d ($R_{CO} = 2.207b$). K -shell electrons are not correlated.

^e ($R_{CO} = 2.132b$). K -shell electrons are not correlated.

Table III. Correlation energies determined by MBPT and CCD methods. Percentage of correlation energy obtained is given in parenthesis

	All electrons			Valence electrons ^a				
	SDQ	MBPT(4)	CCD	EXP ^b	SDQ	MBPT(4)	CCD	EXP ^{b, c}
C	-0.0936 (63%)	-0.0948 (64%)	-0.149	-0.0761 (79%)	-0.0773 (81%)	-0.096		
N	-0.1134 (63%)	-0.1132 (63%)	-0.181	-0.0949 (75%)	-0.0947 (75%)	-0.127		
O	-0.1466 (60%)	-0.1499 (61%)	-0.245	-0.1274 (68%)	-0.1307 (70%)	-0.186		
CH ₄	-0.2124 (72%)	-0.2118 (72%)	-0.293	-0.1929 (81%)	-0.1933 (81%)	-0.240		
NH ₃	-0.2343 (70%)	-0.2334 (69%)	-0.334	-0.2170 (78%)	-0.2161 (77%)	-0.280		
H ₂ O	-0.2480 (68%)	-0.2467 (68%)	-0.365	-0.2297 (75%)	-0.2284 (75%)	-0.396		
CO	-	-	-0.530	-0.3169 (76%)	-0.3097 (74%)	-0.418		
CO ₂	-	-	-0.863	-0.5158 (75%)	-0.5040 (73%)	-0.692		

^a The valence correlation energy is computed for CO and CO₂ by freezing the core electrons. For other cases, the second-order pair correlations involving the 1s² pair are subtracted from the net correlation energy given by the method, to obtain a valence correlation estimate

^b Reference [59]. Also JANAF Thermochemical Tables, National Bureau of Standards. All correlation energies are corrected for zero-point vibration and relativistic corrections.

^c Valence shell correlation energies are obtained from the experimental values by subtracting the 1s², KK and KL shell contributions to the correlation obtained by R. K. Nesbet, Phys. Rev. 175, 2 (1968), for the He isoelectronic sequence.

some cases, such as CO and CO₂ where multiple bonds are involved, second-order can even somewhat over-estimate the infinite-order CCD energy. Note, however, that with the MP splitting, second-order is usually surprisingly close to the CCD result, and as a consequence, is probably a fairly reasonable first estimate of the basis set limit.

Alternatively, if the excited-orbitals are determined within a V^{N-1} potential [6] (i.e., a unity transformation of the excited orbital space) [24, 30, 45, 46], or denominator shifts (6) are used to define a different splitting of the Hamiltonian (e.g., the Epstein-Nesbet partitioning [47]), much lower second-order energies are obtained [15]. In many such cases these energies are close to the "experimental" correlation energy, but since the basis set limit is the only valid objective of the calculation, and since a different separation of the Hamiltonian or a unitary transformation among the excited orbitals cannot change this ultimate result, these modifications will also make the third- and higher-order energies larger to offset the large overestimate in second-order. Since for most finite basis sets the unmodified MP perturbation series seems fairly well-behaved it seems to be preferable. Once CCD or some similar infinite-order result is obtained, there is, of course, no difference and, in fact, this invariance is essentially achieved in low-order [15, 30].

There is some question whether the perturbation series would have the same observed behaviour if one actually had the "true" V^N and V^{N-1} excited orbitals as opposed to their projection onto a limited space. This, of course, is closer to the situation where numerical solutions are obtained as is the case in atomic calculations. In such calculations, the V^{N-1} potential is also a useful aid in performing the numerical integrations since the excited orbitals are constrained from being as diffuse as V^N orbitals [6].

For the open-shell atoms in Table I a UHF reference function is employed. Consequently these solutions are not an eigenfunction of spin. The multiplicity computed from the transition state formula, $\langle \Phi_0 | \hat{S}^2 | \Psi \rangle$, where Ψ is the appropriate correlated wavefunction are also given. In each case the UHF function is a good approximation to the spin state with additional improvement obtained from higher-order perturbation corrections. By monitoring the multiplicity in this manner for open-shell cases, one can be confident that the errors due to spin contamination are not too great. In some cases, particularly for singlet states

where a UHF function is employed to achieve correct separation at large internuclear distances to open-shell fragments (e.g., N₂ as discussed in Section 5) spin contamination is sometimes observed to be quite large suggesting that a UHF based approach is inappropriate.

In fourth-order, in addition to the contributions from single, double, and quadruple excitation diagrams given in Tables I and II, there are the 16 antisymmetrized triple excitation diagrams shown in Fig. 1. Unlike all other diagrams in Fig. 1 and the infinite-order CCD model, whose dependence on the number of basis functions is $\leq N^6$, these diagrams have an N^7 dependence. This makes it impractical to include these terms without additional simplifications. Judging from the fact that the individual components of E_4^{SDQ} have about the same order of magnitude, one expects that the triple excitation terms would also be about the same size. Furthermore, these terms are negative. Hence, the fourth-order contribution shown is actually an upper bound to the full fourth-order result. One hopes, however, that the fourth-order triple-excitation terms will have a relatively small effect on energy differences and may be safely neglected. This is not true for some cases [48], however, and should be investigated.

Even with the triple excitation diagrams neglected, E_4^{SDQ} usually is about the same magnitude as E_3 , and can be larger. This is partially due to the inclusion of new types of excitation diagrams, but even the fourth-order double excitation part, E_4^D , may frequently have a larger magnitude than E_3 ($= E_3^D$). This would seem to imply an asymptotic behaviour to the perturbation series that could be a problem. However, the CCD model tends to support the validity of the fourth-order approximation. In CCD one is summing all double excitation diagrams to all orders and all the linked quadruple excitation energy diagrams that arise from the disconnected wave function component $1/2T_2^2 |\Phi_0\rangle$ plus their mutual coupling [14]. Since this is done in an iterative fashion, convergence to the CCD result is observed. From Tables I and II it is further apparent that DQ-MBPT(4) and CCD are usually quite close.

The near coincidence of DQ-MBPT(4) and CCD is further illustrated in Fig. 2, where a plot of the differences between the two approximations is shown for a wide variety of molecules at their equilibrium geometry. Since chemical accuracy is normally thought to be $\sim 1 \text{ kcal mole}^{-1}$ (0.043 eV), there is

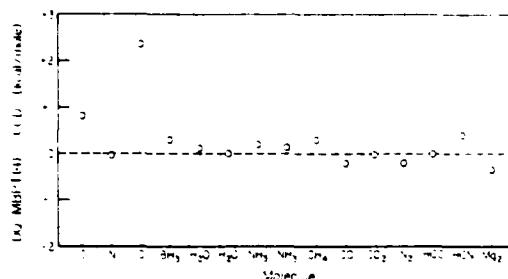


Fig. 2. Illustration of the difference in the energy obtained by DQ-MBPT(4) and CCD for a number of molecules. In the cases where a molecule is listed twice, a different basis set is used. In all cases the basis sets are at least of double-zeta plus polarization quality.

little inaccuracy in using the DQ-MBPT(4) model most of the time. At geometries where the theory is less satisfactory, such as N_2 at some distance beyond equilibrium where a single determinant reference function is inadequate, a difference of ~ 30 kcal mole $^{-1}$ is observed with the CCD result being superior [49]. Since the single excitation terms in fourth-order are not insignificant, one hopes that the SDQ-MBPT(4) results will also be similarly close to results obtained from a CCSD model (i.e., $\psi_{CCSD} = e^{\hat{T}_1 + \hat{T}_2} |\Phi_0\rangle$).

From the foregoing, it is apparent that the quadrupole excitation contributions can be handled within MBPT/CCM. The next logical question is their effect on the correlation energy. The magnitude of this effect may be assessed by considering the difference between the almost coincident CCD or DQ-MBPT(4) energies and the energy obtained by D-CI. Some of these results are shown in Table IV. [Except for H_2O in the STO basis set where we have done the all doubles CI calculations, the VPD-CI(2) model [14] is used for D-CI. This is a variational-perturbation approximation to D-CI that is correct through fifth-order in the energy. In all cases shown here, the VPD-CI(2) results should be within about a percent of the D-CI correlation energy (for H_2O VPD-CI(2) gives 99.9% of D-CI

energy) which is sufficient to make a qualitative assessment of the importance of the quadrupole excitations on the energy.]

The molecules in Table IV are arranged by the number of electrons that are being correlated. From size-extensivity arguments based upon noninteracting electron pairs, one expects the importance of the quadrupole excitation contributions to roughly increase with the number of electron pairs. Other factors, such as the extent of localization, quality of basis set, etc., also affect this trend, but this is basically what is observed from the present examples. The double-zeta basis set used for benzene is not capable of achieving a lot of correlation, but a surprisingly large effect is still observed. Overall, the error due to neglecting quadrupole excitations in CI still amounts to $\sim 20\%$ of the correlation energy even for relatively small molecules. In Section 5, it will be demonstrated that even an effect of 4% due to quadrupole excitations, can still have a definite influence on the accuracy of a potential energy surface [19]. As a consequence, it is frequently unjustified to neglect such higher excitations in CI, and either many-body methods or multi-reference based CI schemes, that would include the more important quadrupole excitations as double-excitations from doubly excited reference determinants, should be encouraged.

In table 5 several MBPT/CCD calculations are shown for H_2O in different sized basis sets. It is apparent that the principal effect of the basis on the correlation energy occurs in second order. The next largest effect is at the SCF level, with third and higher-order being affected by the choice of basis set only at the millihartree (0.63 kcal mole $^{-1}$) level. In fact, after second-order, there is little to choose between a good CGTO basis and a quite complete STO basis set. This is largely due to the fact that the STO basis in this case correlates the core electrons much better than does the CGTO basis, but the higher-order terms are primarily valence correlation contributions. In the case of H_2O good convergence is obtained even for the small ($4s2p/2s$) basis, but for N_2 , for example, convergence is much better in a larger basis set.

Table IV. Effect of quadrupole excitations in CI

	$[(VPD-CI(2))-DQ-MBPT(4)]$ (Kcal/mole)	Percent error in correlation energy
$H_2O (5s3p1d/3s1p) CGTO$	6.2	4.0
$H_2O^* (5s4p2d/3s1p) STO$	7.6	4.2
$B_2H_6^b (4s2p1d/2s1p) CGTO$	10.4	6.2
$CO^b (5s3p1d) CGTO$	12.7	6.5
$HCN^b (4s2p1d/2s1p) CGTO$	14.9	8.2
$CO_2^b (5s3p1d) CGTO$	29.2	9.0
$CH_3CN^b (4s2p1d/2s1p) CGTO$	30.5	11.0
$C_2H_6^b (4s2p/2s) CGTO$	63.6	19.6

^a D-CI is used for comparison in this example.

^b Core electrons are frozen in these examples.

Table V. Basis set effect on components of the correlation energy of H_2O . (All energies in Hartree a.u.)

Basis	E_{SCF}	E_1	E_2	E_3^S	E_4^D	E_5^Q	E_6^{SDQ}	DQ-MBPT(4)	CCD
$1s2p/2s^2$ CGTO	-76.0093	-0.1378	-0.0021	-0.0009	-0.0030	-0.0008	-0.0047	-0.1437	-0.1440
$1s3p1d/2s1p$ CGTO	-76.0478	-0.2411	-0.0037	-0.0015	-0.0039	-0.0022	-0.0032	-0.2465	-0.2467
$1s4p2d/3s1p$ STO	-76.0642	-0.2818	-0.0032	-0.0020	-0.0043	-0.0032	-0.0031	-0.2861	-0.2862
(Estimated SCF Limit - 76.0675)									(Estimated correlation energy - 0.370)

^a Dunning double-zeta basis set [43]. The results for the valence shell correlation energy in this basis through fourth-order have been reported in [34].

^b Slater type orbital basis set of [51]. These results have been reported in [19].

4. Dissociation energies

As discussed in the introduction, one of the primary advantages of many-body methods is their size-extensivity property. This property is a consequence of eliminating all unlinked diagrams in the energy. This feature has the corollary, that the dissociation of closed-shell molecules into closed-shell fragments is also size-consistent in Pople's definition, that is $\lim_{R_{AB} \rightarrow \infty} E(AB) = E(A) + E(B)$. If open-shell fragments are involved, then in the case of a single determinant reference function, a UHF function is usually necessary to ensure correct separation. This imposes a second requirement in addition to using the linked-diagram theorem to obtain size-extensive and size-consistent dissociation to open-shell fragments.

Several thermochemistry results obtained by our group [25, 28, 29] are listed in Table VI. In all reactions except the decomposition of HCO, closed-shell species are separating into closed-shell fragments. Except for the isomerization energy of HNC, it is apparent that the agreement with experiment is excellent. In fact, the calculations are sufficiently accurate that we question the experimental value for $HNC \rightarrow HCN$ rearrangement which will be the subject of another communication [50].

The basis sets used in these calculations are double zeta augmented by polarization functions (for HCO a somewhat larger basis is used.) At this level 60–70 functions are required

to study the borane containing molecules and the methyl-isocyanide rearrangement. These, along with our studies of molecular hyperpolarizabilities [35], are the largest basis MBPT calculations which have been made. As mentioned in Section 2, even though good basis sets still permit large errors in absolute energies, energy differences can be expected to be much better. This is illustrated by the results of Table VI. Of course, the best results would be expected when the fewest bonds are broken.

In Table VII are computed the dissociation energies for the molecules in Table II obtained for decomposition to their atomic constituents. The errors in this case vary from ~ 20 to ~ 80 kcal/mole⁻¹, or about 5–20%. These are compared with results obtained from the VPD-CI(2) method. Even though the VPD-CI method is not size-extensive, and one would normally prefer to obtain dissociation energies in such a CI model by doing a super-molecule calculation for the separated species, the differences in the computed dissociation energies are not that much poorer than that obtained by the various many-body models. Agreement may be further improved by converging to the D-CI result.

5. Potential energy surfaces

The next important question to pose about many-body methods is their reliability for potential energy surfaces. Just as in the

Table VI. Comparison of thermochemistry results obtained by SCF and MBPT with experiment. [All basis sets are (4s2p1d 2s1p) except for HCO where a (4s3p1d 3s1p) basis is used]

Reaction	Method	- ΔE (kcal/mole)			Experiment
		SCF	MBPT/CCD		
$2BH_3 \rightarrow B_2H_6^a$	SDQ-MBPT(4)	18.5	35.6	36.6 \pm 2 ^d	
$BH_3 + CO \rightarrow H_3BCO^a$	D-MBPT(4)	8.0	20.5	20.4 \pm 2 ^d	
$BH_3 + NH_3 \rightarrow H_3BNH_3^a$	D-MBPT(4)	20.5	30.1	—	
$HNC \rightarrow HCN^b$	SDQ-MBPT(4)	9.7	14.7	(10.3 \pm 1) ^e	
$HNC \rightarrow [H_2N]^b$	SDQ-MBPT(4)	-34.6	-30.9	—	
$CH_3NC \rightarrow CH_3CN^b$	SDQ-MBPT(4)	19.2	22.8	23.7 \pm 0.14 ^f	
$CH_3NC \rightarrow [CH_3NCl]^b$	SDQ-MBPT(4)	-44	-40	-38.4 ^g	
$H + CO \rightarrow HCO^e$	CCD	4.8	13.7	15.7 \pm 1.5 ^h	
$HCO \rightarrow [HCO]^e$	CCD	-12.8	-18.2	—	

^a Reference [29].

^b Reference [25]. Square bracket indicates a transition state. This result includes a 4 kcal/mole zero point correction for the transition state.

^c Reference [28]. Square bracket indicates a transition state. This result includes a 4.8 kcal/mole zero point correction for the transition state.

^d Fehlner, T. P. and Mappes, G. W., *J. Phys. Chem.* **73**, 873 (1969).

^e Maki, L. (unpublished results).

^f Baghal-Vayjovec, M. H., Collister, J. L. and Pritchard, H. O., *Can. J. Chem.* **55**, 2634 (1977).

^g Schneider, F. W. and Rabinovitch, B. S., *J. Am. Chem. Soc.* **65**, 1794 (1969).

^h Warneck, P., *Z. Naturforsch.* **A26**, 2047 (1971).

Table VII. Predicted dissociation energies, D_e , from different methods (energies are kcal/mole)^a

Method	CH_4	NH_3	H_2O	CO_2	CO	$CO_2 \rightarrow CO + O$
SCF	324.71	195.20	151.14	240.22	170.19	70.03
MBPT(2)	397.06	272.11	217.40	349.70	232.82	116.89
MBPT(3)	399.76	270.64	213.66	315.04	214.01	101.04
D-MBPT(4)	399.90	271.54	214.66	317.63	215.91	101.73
SD-MBPT(4)	400.38	272.20	215.35	324.41	219.89	104.53
SDQ-MBPT(4)	399.25	271.16	214.77	321.11	218.30	102.82
DQ-MBPT(4)	398.74	270.41	214.07	314.31	214.30	100.01
CCD	398.10	270.63	211.83	308.82	210.94	97.88
Exp ^b	419.49	297.25	232.37	388.68	258.85	129.83
VPD-CI(2)	392.75	264.84	209.38	288.05	202.97	85.08

^a Dissociation is to ground state atoms in each case, $CH_4 \rightarrow C(^3P) + 4H(^1S)$, except where indicated otherwise.

^b Reference [59]. Also JANAF Thermochemical Tables, National Bureau of Standards.

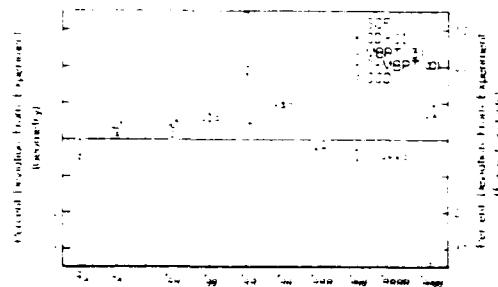


Fig. 3. Percent deviation of theoretical from experimental values for the equilibrium geometry (left scale) and force constants (right scale) of the water molecule. Experimental values are from Hoy, Mills, and Strey (Mol. Phys. 24, 1265 (1972)) and, where available, from the revised fit by Hoy and Bunker (J. Mol. Spectrosc. 74, 1 (1979)). Theoretical methods employed are Hartree-Fock (SCF), all single and double excitation configuration interaction (SD-CI), and the many-body perturbation theory (MBPT) methods: at third order (MBPT(3)), at infinite order including double excitation type diagrams only (D-MBPT(∞)), and coupled cluster doubles (CCD). Technical details of the methodologies are given in [14]. Agreement between theory and experiment is best for points located nearest the central horizontal line.

case of dissociation energies, relative energy differences are important and one hopes that calculations in sufficiently flexible basis sets will benefit from substantial cancellation of the innate basis set error. However, unlike dissociation energies where only a few points are required, the details of the shape and curvature of the surface still place stringent requirements on the basis set due to the fine energy differences that occur among the many computed geometries.

In our work, we have studied two triatomic energy surfaces [19, 28] in depth and various diatomic potential energy curves [14, 26, 27, 49]. Of these, our study of the H_2O molecule [19] in a very good Slater orbital basis set ($5s4p2d/3s1p$), defined by Rosenberg and Shavitt [51], is particularly informative. The objective of this study is to investigate the quartic force field of H_2O with CCD, MBPT, SD-CI, and SCF by performing calculations at 36 points, involving symmetric and asymmetric geometries [19, 52]. All points are located within the zero vibrational displacement.

The results of the prediction of the bond length and bond angle and several of the quartic constants for H_2O are illustrated in Fig. 3 [19]. The center line represents the experimental values as determined by Hoy, Mills, and Strey [53], and as revised by Hoy and Bunker [54]. It is apparent that the trend in the errors is typically SCF > SD-CI > MBPT(3) > CCD > D-MBPT(∞). Had the SDQ-MBPT(4) results been included on the figure they would typically fall between CCD and D-MBPT(∞) [19].

The determination of force constants from analysis of the infra-red spectrum and the subsequent normal coordinate analysis does not always provide an unambiguous force field. Hence, better agreement with experiment does not necessarily imply the superiority of the many-body methods to SD-CI. (The most appropriate comparison would be the full CI in the specified basis set.) Furthermore, in rigor, CCD should be superior to D-MBPT(∞), but the neglect of single- and triple-excitation diagrams in the CCD model, which would lower the energy compared to CCD, would result in energies much closer to those given by D-MBPT(∞). This is also supported by the observation that SDQ-MBPT(4) which includes the single excitation effects, is usually in a little better agreement with experiment than CCD

Table VIII. Comparison of predicted geometries of the formyl radical (HCO) with experiment

	R_{O}^{CH} (Å)	R_{C}^{CO} (Å)	θ , (Degrees)
RHF ^a	1.098	1.188	130.0
UHF ^b	1.099	1.157	126.8
D-MBPT(4) ^b	1.111	1.188	124.0
Experiment ^c	1.125	1.175	124.95

^a Bruna, P. J., Bunker, R. J. and Peyerimhoff, S. D., J. Mol. Structure 32, 217 (1976).

^b Reference [28].

^c Brown, J. M. and Ramsey, D. A., Can. J. Physics, 53, 2232 (1975).

[19]. Hence, the slightly better agreement with experiment of D-MBPT(∞) tends to be a result of some error cancellation [19].

The current results, though certainly not definitive, are strongly suggestive that the inclusion of some effects of quadrupole and higher even ordered excitations as in the many-body methods, CCD, SDQ-MBPT(4), and D-MBPT(∞), is important in obtaining highly accurate potential energy surfaces even near equilibrium. (This is not an isolated observation since even Davidson's CI estimate of the quadrupole excitation contribution [55-58] has been found to have an improved effect on potential energy surfaces [51, 60].) To some degree, this may be understood by recognizing that quadrupole excitations like $(1b_2)^2(3a_1)^2 \rightarrow (4a_1)^2(2b_2)^2$ are required for proper dissociation of H_2O into $\text{O}({}^3\text{P})$ and $2\text{H}({}^2\text{S})$ [52], and this effect, is apparently felt all the way into the well of the H_2O surface [19].

The decomposition reaction of the formyl radical, $\text{HCO} \rightarrow \text{H} + \text{CO}$ has also been studied [28], including a determination of the transition state and an estimate of the rate constant for this system [28, 61]. This differs from the H_2O example in that the formyl radical is an open-shell species and one is interested in the surface all the way to dissociation. For both reasons, it is useful to use a UHF reference function in this study.

Potentially, UHF functions have a number of problems. Besides their failure to be spin eigenfunctions, they may also converge to different symmetry broken solutions at different geometries sometimes making it difficult to use these functions in surface studies. In the case of HCO where only the single bond is broken, this turns out not to be much of a problem, however.

The full surface is studied at the level of D-MBPT(4) with CCD results being determined at certain critical points. As in H_2O [19], only minute differences between D-MBPT(4) and CCD were observed in this example [28]. (In more complicated cases where one determinant is not a good zeroth-order approximation, CCD and D-MBPT(4) can differ more significantly [14].)

We find that for the full extent of the surface the D-MBPT(4) corrected multiplicity varies from 2.000 at infinite separation of H and CO to 2.02 at the saddle point, decreasing somewhat as one moves toward the equilibrium structure of the radical. As in the case of H_2O , the geometry of HCO shown in Table VIII obtained by the relatively simple D-MBPT(4) model tends to be in excellent agreement with experiment [28].

One final example illustrates the important deficiencies of the current single determinant reference function MBPT CCD methods. It is well-known that an RHF function will not separate correctly at large R for the vast majority of molecules.



Fig. 4. UHF and RHF N_2 potential energy curves compared to experiment. The minima of the curves are superimposed. The UHF curve is lower in energy than the RHF curve at all R .

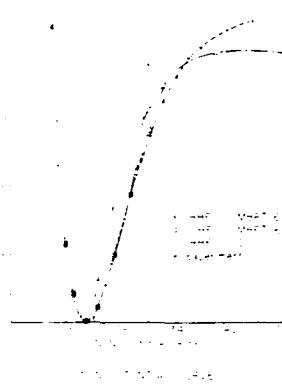


Fig. 5. (UHF) and (RHF)-D-MBPT(6) and (RHF) CCD potential energy curves for N_2 . The minima of the curves are superimposed. The D-MBPT(6) correlated UHF curves are higher in energy than the D-MBPT(6) RHF curves between $R = 2.0$ Bohr and $R = 2.7$ Bohr. The (RHF)-CCD result extends the reliability of the curve over the (RHF)-D-MBPT(6) approximation to somewhat larger R values.

and consequently, as a reference function for MBPT/CCM, this incorrect behavior must eventually manifest itself. A UHF wavefunction will generally, (but not always) separate correctly, but from spin contamination and other problems associated with different broken symmetry solutions, the UHF function may exhibit incorrect behavior on its path toward separation. This, too can persist even with correlation included.

These features are illustrated in the N_2 potential curve shown in Figs. 4 and 5 [49]. The minimum of the curves are superimposed to illustrate the differences as much as possible. The spin multiplicity of the UHF N_2 solutions is found to be ~ 3.5 even though a singlet state is desired. This is indicative of an enormous contamination from the low-lying triplet, quintet and septet states. From Fig. 5, it is evident that this curious behavior of the UHF solution persists into the correlated calculation. Whereas the correlated RHF calculation gives quite good agreement with the experimental curve as far as it can be expected to apply, the UHF correlated calculation shows almost a reverse curvature only becoming reasonable near the separated atom limit.

A problem of this type demands some type of multireference function based many-body approach as developed by Brandow [36], Lindgren [37], and others [38]. As the N_2 triple bond begins to break, more than one configuration (in a CI description) becomes quite important in the wavefunction, and these extra configurations cannot justifiably be treated by perturbation theory. Preferably, all the configurations that are required for proper dissociation of N_2 (~ 8) should be included in a reference (model) space, of p dimension, with the remainder contributing as the projection manifold of perturbation theory.

There are two interrelated problems with this multireference approach. Since each of the p^2 elements of the effective Hamiltonian matrix requires a computation roughly equal to a full MBPT CCM calculation with a single reference, the computational difficulty rises rapidly the more configurations that need to be included in the model space. Also, if we consider a polyatomic molecule and want to employ all the configurations needed to obtain correct separation for all possible decomposition channels, the dimension, p , can become quite large. We have pursued a somewhat different approach to this problem which is described in a contribution to be published [62].

6. Dipole moments, polarizabilities, and hyperpolarizabilities

To address the question of MBPT CCD studies of properties other than the energy, we have investigated the dependence of a molecule to an external electric field [35]. The expansion of the energy in an electric field E , is

$$H(E) = H(0) - \mu_i E_i - 1/2! \alpha_{ij} E_i E_j - 1/3! \beta_{ijk} E_i E_j E_k - 1/4! \gamma_{ijkl} E_i E_j E_k E_l - \dots \quad (8)$$

Summation over repeated indices is assumed. The coefficients in this expansion are the dipole moment, μ , the polarizability tensor, α , and the second- and third-order (hyper) polarizabilities, β and γ [63].

The importance of μ and α in molecular theory is well-known, while the β and γ hyperpolarizabilities are ultimately responsible for the nonlinear optical effects of molecules [63]. The most intriguing aspect of the latter quantities, is that the nonlinear optical effects can be exploited to make an atomic or molecular gas frequency multiply laser radiation. As such, a knowledge of hyperpolarizabilities (preferably, as a function of frequency), can contribute to a number of potential laser devices of unusual capabilities. The β and γ tensors can be determined by experiments employing second- and third-harmonic generation techniques [64], and by using the Kerr effect [65]. However, the experiments are difficult, the range of uncertainty is large, and in many cases values for β and γ determined by different experimental techniques differ markedly, with even opposite signs obtained in the case of the $\beta = (\beta_{zzz} + \beta_{zxx} + \beta_{zyz})$ hyperpolarizability for some molecules [64b].

A first principle prediction of quantities like hyperpolarizabilities places extreme demands on any quantum mechanical method. Since these quantities, unlike the energy, depend upon the long-range behavior of the charge density, great care must be taken to generate a basis set that can adequately describe this region. Also, unlike α , few bounding properties can be usefully applied to the higher polarizabilities. Finally, correlation is expected to be crucial to determining the sensitive differences in the charge densities that are requisite in a predictive theory of higher polarizabilities.

Employing the Hamiltonian,

$$H = \sum_i (h(i) + V^N(i) - \mu(i) \cdot E) + \sum_{i>j} \mu(i,j)^{-1} - \sum_i V^N(i) \quad (9)$$

$$H = H_0(E) + V_{12} - V^N(E) = H_0(E) + V(E) \quad (10)$$

the energy in the presence of the field is given by

$$W(E) = W_{\text{CHF}}(E)$$

$$+ \sum_{n=1}^{\infty} \langle \Phi_0(E) | V(E) | (E_0(E) - H_0(E))^{-1} V(E) | \Phi_0(E) \rangle_L \quad (11)$$

The quantity, $W_{\text{CHF}}(E)$ is the coupled-Hartree-Fock result. Equations (9-11) can be solved by conventional perturbation theory where all quantities including the V^N potential are expanded in a Taylor's series in the external field. Considering an $H_0(E)$ in this manner, one obtains the so-called coupled perturbed Hartree-Fock (CPHF) result [66, 67]. The additional correlation effects would have to be evaluated by considering the classes of diagrams with one, two, and more interactions with the external field. Also, if one uses this double perturbation approach, one would have to distinguish between the CPHF diagrams and the "true" correlation diagrams in the linked-diagram expansion [67].

Alternatively, finite field techniques may be employed where the HF-SCF equation and the linked-diagram expansion are evaluated, at several small finite-field strengths, from which numerical differentiation provides the various components of the dipole moment and polarizabilities. In the latter case, the solutions of $H_0(E)$ at various field-strengths provides the coupled-Hartree-Fock result, which is equivalent to CPHF [68]. The correlation corrections can be added by evaluating the linked-diagrams as shown in Fig. 1, but now subject to field dependent orbitals. (Note, since all finite-field orbitals are still determined in the appropriate $V^N(E)$ potential, the associated Hartree-Fock cancellations still apply, so no non-Hartree-Fock diagrams need to be evaluated.) The finite-field procedure has the advantage that all the coefficients in eq. (8) can be obtained simply by making enough finite-field energy calculations. This permits using the programs and methods developed for the usual correlation problem which usually offer a more sophisticated level of treatment of the correlation than would be convenient to develop for each order in an external perturbation. Also, there is a natural dichotomy into HF-SCF and correlation effects. The disadvantage is that several different finite-field values need to be considered to obtain the components of the various tensors, and, of course, one must maintain high numerical accuracy in every stage of the computation in order to obtain meaningful numerical derivatives.

In Table IX some results for the HF molecule are displayed. These are the first correlated studies of hyperpolarizabilities which have been reported [35]. The very large basis set ($1s5p4d:5s3p$) was chosen essentially by following the prescription advocated by Christiansen and McCullough [69] who used this scheme to obtain contracted Gaussian orbital basis sets which provided good agreement with completely numerical coupled Hartree-Fock calculations of μ_z , α_{zz} , β_{zzz} , and γ_{zzzz} . With our basis set, agreement with the numerical CHF results in almost perfect for μ_z , and α_{zz} , within 3% for β_{zzz} and 12% for γ_{zzzz} [35].

Correlation at the SDQ-MBPT(4) level has a significant effect on μ and α , bringing the results into very good agreement with

Table IX. Dipole moment, polarizability, hyperpolarizability of HF / basis / $1s5p4d:5s3p$ / all results are in atomic units/

	CHF	SDQ-MBPT(4)	Experiments
μ	0.758	0.709	0.70 ^a
$\alpha = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$	4.89	5.58	5.52 ^b
$\alpha_x - \alpha_z$	1.28	1.21	1.32 ^c
$\beta = (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})$	-8.5	-19.9	-
γ_{zzzz}	280	390	-
γ_{yyzz}	80	140	-

^a Muenster, J. S. and Kemperer, W., J. Chem. Phys. 52, 6033 (1970).

^b Werner, H. J. and Meyer, W., Mol. Physics 31, 855 (1976). Zero-Point Correction to r_e included.

^c Muenster, J. S., J. Chem. Phys. 56, 5409 (1972).

experiment. In the case of β , there is a marked change due to correlation, more than doubling the CHF result. Similarly, the components of γ are increased by 40% and 75%. It is apparent that correlation is absolutely crucial to a predictive theory of these quantities.

It is encouraging that the SDQ-MBPT(4) model seems to be rather accurate for μ and α in this example. It is well known that the single-excitation contributions to properties other than the energy are quite important. This is also true in the present case. The bulk of the single-excitation effects is included in the initial CHF results in the present approach, since as shown by Caves and Karplus, CHF (or CPHF) sum certain categories of single and double-excitation diagrams in the double perturbation approach to all orders [67]. Even so, the residual effects of the single excitation diagrams appearing in the fourth-order energy are still significant [35]. On the other hand, quadrupole excitation diagrams make almost no contribution to these properties. A superior model to SDQ-MBPT(4), is probably a model such as SD-MBPT(∞) or even CCSD that would include the contribution of such single excitation terms to all orders.

7. Conclusions

We believe it has been demonstrated that MBPT CCM can be usefully employed in a wide variety of chemically interesting problems. Within good CCTO or STO basis sets, geometries and local force fields may be predicted very accurately in most cases. Some properties other than the energy can also be obtained to a high degree of accuracy. Dissociation energies in the examples described and others not yet published [70], can be expected to be highly reliable if only a single bond is broken, becoming less so when comparable dissociation to atomic fragments is required. In the latter case, however, the largest error is due to basis set defects rather than any inherent weakness in the methods.

The most glaring failure of MBPT/CCM as implemented in this paper occurs due to the inapplicability of a single determinant reference function. This is the problem in the N_2 example cited, and will remain a problem for a number of potential curves when multiple bonds are broken, in some excited states, and for the general open-shell case. The most encompassing solution to this problem lies in multireference based many-body methods [36-38]. A new approach of this type which has many desirable features is described in a forthcoming paper [62].

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APPENDIX B

A FULL COUPLED-CLUSTER SINGLES AND DOUBLES MODEL,
THE INCLUSION OF DISCONNECTED TRIPLES

A FULL COUPLED-CLUSTER SINGLES AND DOUBLES MODEL,
THE INCLUSION OF DISCONNECTED TRIPLES⁺

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ABSTRACT

The coupled cluster singles and doubles model (CCSD) is derived algebraically, presenting the full set of equations for a general reference function explicitly in spin-orbital form. The computational implementation of the CCSD model, which involves cubic and quartic terms, is discussed and results are reported and compared with full CI calculations for H₂O and BeH₂. We demonstrate that the CCSD exponential ansatz sums higher-order correlation effects efficiently even for BeH₂ near its transition state geometry where quasidegeneracy efforts are quite large, recovering 98% of the full CI correlation energy. For H₂O, CCSD plus the fourth-order triple excitation correction agrees with the full CI energy to 0.5 kcal/mole. Comparisons with low order models provide estimates of the effect of the higher order terms $T_1 T_2$, $T_1^2 T_2$, T_1^3 , and T_1^4 for the correlation energy.

I. INTRODUCTION

Recently, a number of applications of many body perturbation theory (MBPT)⁽¹⁻⁴⁾ and coupled cluster methods (CCM)⁽⁵⁻⁸⁾ to the ab initio calculation of the electronic structure of molecules have been reported.⁽⁹⁾ These applications have restricted the full MBPT/CCM model to a fixed level of perturbation (e.g., third or fourth order as in D-MBPT(3) and SDQ-MBPT(4)) or to including all orders of the class of double excitation cluster operators as in coupled cluster doubles (CCD), or (poorer) the linearized L-CCD(= D-MBPT(∞)) form. The methods implemented usually presume the use of Hartree-Fock orbitals, although this is not necessary.

Here we report the derivation and the computational implementation of the full CCSD model. The method, as implemented, uses any orthogonal set of orbitals and is not restricted to Hartree-Fock orbitals. In particular, it is possible to use symmetrically orthogonalized bond orbitals instead of Hartree-Fock orbitals and to take advantage of the concomitant reduction in the number of molecular integrals in large molecules which results from the more localized structure of the bond orbitals. Additional applications for non-Hartree-Fock orbitals, such as optimizing orbitals so that the energy becomes stationary, are easily envisioned.

There are a number of reasons to recommend the development of the CCSD method as a basis for what Pople calls a "theoretical model chemistry."^(10,11) These criteria propose that a method⁽¹⁾ should be "size-extensive," which means it scales properly with molecular size:

- (2) applicable to a wide range of problems within a single framework;
- (3) invariant to classes of unitary transformations; (4) efficient; and,
- (5) able to correctly separate a molecule into its fragments.

CCSD is a many-body method built upon the linked-diagram theorem. Hence, it is size-extensive; and, in particular, CCSD gives the correct result for the characteristic problem of separated electron pair bonds as in a lattice of N noninteracting H_2 molecules. As long as a single determinant, which need not be a restricted or unrestricted Hartree-Fock function, is a reasonable starting point, CCSD is applicable to most problems without modification or special symmetry conditions.

Furthermore, CCSD is invariant to any transformation among the excited orbitals or the occupied orbitals, respectively. CCSD is not generally invariant to transformations that mix occupied and unoccupied orbitals among themselves. However, for the special case of noninteracting separated electron pairs, it is even invariant to such general transformations. This follows from the fact that CCSD is the "full" CI (i.e., all possible contributing n -tuple excitations of n electrons) for such a model problem. Since interpretations of chemistry are largely based upon the concept of separated electron-pair bonds this is a very desirable aspect of the CCSD model. In a real molecule, different choices of the molecular orbitals will give different energies, but we would expect a smaller effect due to such transformations for CCSD than in less complete models. It will be interesting to see if localized orbital models will be approximately invariant.

The condition of efficiency also recommends CCSD since the treatment of the electron correlation grows no more rapidly than the sixth power of the number of basis functions, M^6 . Thus, CCSD involves no more

coefficients than the configuration interaction single and double excitation model, SD-CI; and, in principle, it is no more time consuming. This is true, even though CCSD includes contributions of quadruple excitations, as well as additional parts of the triple and higher excitations that arise due to disconnected products of single and double excitations. Any attempt to exceed the CCSD model by including higher categories of excitation operators such as the connected triple excitations, T_3 , will invariably result in a model where the number of operations would asymptotically rise more rapidly than M^6 .

The condition of correct separation depends upon the reference function as well as the degree of correlation included and generally requires the resolution of degeneracy problems. Full CI with a single reference function obviously separates correctly even for poor choices of reference function. For less complete correlation models, the relative importance of the reference function and the correlation corrections is not yet determined, often recommending multireference techniques. A single UHF function will, in general, separate correctly, though it can suffer from large amounts of spin-contamination causing an erroneous behavior of a potential energy surface. With any choice of reference function, CCSD will certainly go farther toward achieving correct separation than SD-CI, so we might expect a higher level of applicability. For example, CCD is known to correctly handle some severely degenerate problems,^(12,13) and in this paper, CCSD is similarly shown to resolve two highly degenerate problems without resorting to multireference function techniques. Consequently, CCSD offers a potentially attractive model for a "theoretical model chemistry" that can often even achieve correct separation or resolve some kinds of degeneracies despite employing a single reference configuration.

In the following section we will review coupled-cluster theory and the singles and doubles approximation. Section III summarizes the CCSD equations and Section IV sketches the method of implementation. Finally, Section V compares CCSD calculations at the double zeta level on H_2 , H_2O , and BeH_2 with full-CI calculations.

II. THE SINGLE AND DOUBLE EXCITATION APPROXIMATION IN COUPLED CLUSTER THEORY

Coupled cluster (CC), many-body perturbation theory (MBPT), and configuration interaction (CI) are methods designed to solve the Schrödinger equation, and consequently, all can be interrelated. The primary difference is in how higher order excitation configurations are handled, with the consequence that many-body methods are size-extensive. In particular, CC theory can be viewed as a way to sum certain categories of many-body perturbation theory diagrams to all orders. While such a viewpoint has advantages, we will discuss the CCSD approximation from the viewpoint of an exponential representation of the exact wavefunction. That is, we will write the exact solution to the Schrödinger equation as an exponential of the cluster operator operating on a reference function,⁽⁷⁾

$$\psi_{\text{exact}} = \psi_{\text{CC}} = e^{\hat{T}} \phi_0 \quad (1)$$

where ϕ_0 is a single determinant and \hat{T} is a cluster operator which is usually separated into one-body, two-body, etc. cluster contributions.

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots \quad (2)$$

The various parts of the cluster operators are represented as expansions of second quantized excitation operators and the problem of determining \hat{T} is reduced to the problem of finding the expansion coefficients of the second quantized operators. For \hat{T}_1 and \hat{T}_2 , the expansions are

$$\hat{T}_1 = \sum_{i,a} t_i^a a_a^\dagger a_i \quad (3)$$

and

$$\hat{T}_2 = \sum_{\substack{i>j \\ a>b}} t_{ij}^{ab} a_a^+ a_i^+ a_b^+ a_j \quad (4)$$

where we have adopted the convention that the lower case Roman subscripts (superscripts) i, j, k, ℓ, \dots (a, b, c, d, \dots) refer to orbitals which are occupied (unoccupied) in the reference determinant. The undetermined coefficients are $\{t_i^a\}$ and $\{t_{ij}^{ab}\}$ while $\{a_a^+ a_i^+\}$ and $\{a_a^+ a_i^+ a_b^+ a_j^+\}$ are second quantized sets of single and double excitation operators, and t_{ij}^{ab} is antisymmetric (i.e., $t_{ij}^{ab} = -t_{ji}^{ab} = -t_{ij}^{ba} = t_{ji}^{ba}$).

The chief advantage of CC over CI can be easily demonstrated by using the expansion of an exponential operator,

$$e^{\hat{T}} = 1 + \hat{T} + \frac{1}{2} \hat{T}^2 + \frac{1}{6} \hat{T}^3 + \dots \quad (5)$$

to bring the CC cluster operators into a formal correspondence with the CI excitation operators. In the CI method, the exact wave function can be written as a linear combination of excitations from a reference determinant.

$$\psi_{\text{exact}} = \psi_{\text{CI}} = (1 + \hat{C}_1 + \hat{C}_2 + \dots \hat{C}_N) \phi_0 \quad (6)$$

where \hat{C}_i is a sum of i -fold excitations with coefficients which must be determined. The correspondence between \hat{C}_i 's and \hat{T}_i 's is established by using equations (2) and (5) in (1) to produce an expanded equation

$$\psi_{\text{exact}} = (1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots + \frac{1}{2} \hat{T}_1^2 + T_1 T_2 + \frac{1}{2} \hat{T}_2^2 + \dots) |s_0 \rangle \quad (7)$$

Terms with the same total excitation level are collected together and equated to the CI coefficient of the same excitation level. For example, the CI quadruple excitations, $\hat{C}_4\phi$, correspond to the following sum

$$\hat{C}_4 = \hat{T}_4 + \frac{1}{2}\hat{T}_2^2 + \hat{T}_1\hat{T}_3 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{4!}\hat{T}_1^4. \quad (8)$$

Thus, CC can be regarded as a way to decompose CI coefficients into other, possibly more physically meaningful terms.⁽¹⁴⁾ In the case of quadruples, a substantial body of work has indicated that the largest component of \hat{C}_4 comes from $\frac{1}{2}\hat{T}_2^2$ in equation (8).⁽¹⁴⁻¹⁶⁾ From a computational point of view, this is an important observation because the effects of \hat{T}_2^2 can be included using algorithms where the work is proportional only to the sixth power of the basis set size instead of proportional to the eighth power of the basis size.

The CCSD method is an approximate CC method in which the exact wave function (c.f. equation (1)) is approximated by truncating the expansion of \hat{T} (c.f. equation (2)) after \hat{T}_2 . Thus,

$$\psi_{\text{exact}} \approx \psi_{\text{CCSD}} = e^{\hat{T}_1 + \hat{T}_2} \phi_0. \quad (9)$$

The coefficients which must be determined are just those given in equations (3) and (4), and the number of unknown coefficients in the CCSD approximation equals the number of coefficients in SD-CI. Thus, the level of computational effort required in the CCSD model is expected to be comparable to the level of effort required for the SD-CI model. However, as indicated in equation (8), the CCSD approximation incorporates parts of the CI quadruple excitation terms, namely, $\frac{1}{2}\hat{T}_2^2$, $\hat{T}_1\hat{T}_3$, and $\frac{1}{4!}\hat{T}_1^4$, and it does so more economically and

compactly than a SDQ-CI calculation can. There is evidence based upon perturbation theory, previous calculations and physical grounds that the single missing term, \hat{T}_4 , is usually not needed to achieve accurate calculations.⁽¹⁴⁻¹⁸⁾ In addition to including the effects of CI-type quadruple excitations, the CCSD model also incorporates some of the effects of triple excitations. Associating \hat{C}_3 with cluster terms, we find

$$\hat{C}_3 = \hat{T}_3 + \hat{T}_1 \hat{T}_2 + \frac{1}{3!} \hat{T}_1^3 \quad . \quad (10)$$

Thus, the CCSD model incorporates the $\hat{T}_1 \hat{T}_2$ and \hat{T}_1^3 components of CI type triple excitations. Unfortunately, when Hartree-Fock orbitals are used, perturbation theory indicates that the dominant contribution to \hat{C}_3 usually comes from \hat{T}_3 ,⁽¹⁶⁻²¹⁾ which is not included in the CCSD method. On the other hand, if non-Hartree-Fock orbitals are used, so that \hat{T}_1 is large, then the dominant contributions to \hat{C}_3 can come from $\hat{T}_1 \hat{T}_2$ and \hat{T}_1^3 . In practice, we have found that these terms do become important in bond breaking processes which one is usually tempted to describe with a multireference approach. They seem to remain unimportant for simple closed-shell molecules at their minimum energy geometries. As in the case of the \hat{C}_4 components inherent in CCSD, the disconnected \hat{C}_3 components can be computed with algorithms in which the work is proportional to the sixth power of the size of the basis set.

III. CCSD EQUATIONS

The procedure for deriving the CCSD equations have been previously reported in diagrammatic form⁽⁷⁾ and approximations to these equations in orbital form,⁽¹⁶⁾ using elegant and compact notations.

In some cases the reported equations have been restricted to Hartree-Fock orbitals or approximations were made in the equations. In this section we present the complete set of equations satisfied by the coefficients which define \hat{T}_1 and \hat{T}_2 in the CCSD method. These equations are applicable to any set of orthonormal spin-orbitals. In particular, the equations are applicable to RHF and UHF as well as non-Hartree-Fock reference determinants. The equations are derived algebraically for this work using the conventional procedure beginning with the Schrödinger equation

$$(H - E_{CCSD}) \psi_{CCSD} = (H - E_{CCSD}) e^{\hat{T}_1 + \hat{T}_2} |\phi_0\rangle = 0 \quad (11)$$

and projecting onto a set of functions, $\langle \phi_0 |$, $\langle i^a |$, and $\langle ij^{ab} |$, such that a set of equations sufficient for determining the t_i^a and t_{ij}^{ab} coefficients results,

$$\langle \phi_0 | (H - E_{CCSD}) | e^{\hat{T}_1 + \hat{T}_2} \phi_0 \rangle = 0 \quad (12)$$

$$\langle i^a | (H - E_{CCSD}) | e^{\hat{T}_1 + \hat{T}_2} \phi_0 \rangle = 0 \quad \text{for all } i, a \quad (13)$$

$$\langle ij^{ab} | (H - E_{CCSD}) | e^{\hat{T}_1 + \hat{T}_2} \phi_0 \rangle = 0 \quad \text{for all } i, j, a, b \quad (14)$$

Next, the exponential is expanded using equation (5) and using the fact that H contains no more than two-electron operators, we have

$$\langle \phi_0 | H - E_{CCSD} (1 + T_1 + T_2 + \frac{1}{2} T_1^2) | \phi_0 \rangle = 0 \quad (12a)$$

$$\langle i | H - E_{CCSD} (1 + T_1 + T_2 + \frac{1}{2} T_1^2 + T_1 T_2 + \frac{1}{3} T_1^3) | \phi_0 \rangle = 0 \quad (13a)$$

$$\langle ij | H - E_{CCSD} (1 + T_1 + T_2 + \frac{1}{2} T_1^2 + T_1 T_2 + \frac{1}{2} T_2^2 + \frac{1}{2} T_1^2 T_2 + \frac{1}{3} T_1^3 + \frac{1}{4} T_1^4) | \phi_0 \rangle = 0 \quad (14a)$$

Evaluating (12) in terms of the amplitudes t_i^a and t_{ij}^{ab} , then gives

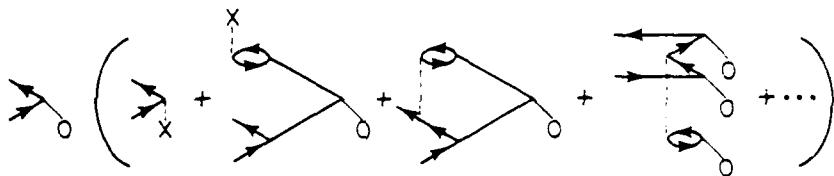
$$E_{CCSD} = \langle \phi_0 | H | \phi_0 \rangle + \sum_{ia} f_{ia} t_i^a + \sum_{\substack{i>j \\ a>b}} \langle ij || ab \rangle (t_{ij}^{ab} + t_{ij}^{a b} - t_{ij}^{a b}) \quad (15)$$

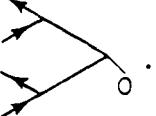
where $f_{ia} \equiv \langle i | H | \phi_0 \rangle$ and $\langle ij || ab \rangle = j x_i^*(1) x_j^*(2) \frac{(1-p_{12})}{r_{12}} x_a(1) x_b(2) d\tau_1 d\tau_2$

Finally, equation (15) is substituted into equations (13) and (14) causing terms, which would make unlinked contributions to the energy, to cancel and eliminating the explicit E dependence of the t coefficients. The other important step in the derivation is to observe that the T_1 equation may be factored from the equation for the T_2 amplitude, as discussed more fully, below. Evaluating the resulting second-quantized matrix elements with KOMMUTE⁽¹⁷⁾, a computer program for determining matrix elements between determinants, and carrying out the above simplification results in the two equations satisfied by the amplitudes in \hat{T}_1 and \hat{T}_2 . These are presented in Tables (1, 2, 3). After solving the equation of Tables 1-3 the energy is given by Eq. (15).

An important aspect of the coupled cluster equations, in general, and the CCSD equations in particular are their fully "connected" diagrammatic form. All unlinked diagrams (diagrams that contain a closed disconnected

part) cancel with the energy in Eqs. (13-14), thereby ensuring the size-extensivity of the model.⁽¹⁸⁾ Disconnected diagrams (diagrams that have open disconnected parts) would still remain in the general case. However, Lindgren⁽¹⁸⁾ has proven that in coupled cluster theory, only connected diagrams need be considered for the various T_n amplitudes. This feature becomes transparent in the direct algebraic derivation presented here, since all disconnected diagrams obtained in the straightforward evaluation of Eq. (14) correspond to a single particle amplitude, t_i^a multiplied by the T_1 equation of Table 1, which, of course, vanishes. Diagrammatically, these disconnected terms are of the form



where a T_1 amplitude is signified by  and a T_2 amplitude by .

A recent thesis by Cullen,⁽¹⁹⁾ presents the diagrammatic deviation of the CCSD equations with a thorough enumeration of the diagrams.

Several points about the expressions for the T_1 and T_2 amplitudes should be made. First, at this point we have not yet prescribed a method for solving these equations. Second, the equations are nonlinear and coupled, a feature they share with the Hartree-Fock or MCSCF equations. Third, the equations are quartic in \hat{T}_1 but only quadratic in \hat{T}_2 . The quadratic nonlinearities are similar to the nonlinearity that is implicit in the CI secular problem (see Appendix). Although the quartic nonlinearity can be a problem, anyone who has solved Hartree-Fock or MCSCF problems is unlikely to be deterred by the comparatively low level of nonlinearity in the CCSD equations. A fourth feature is that the computational effort required to evaluate each amplitude grows asymptotically no more rapidly than the sixth power of the number of basis functions. In a system with n occupied orbitals and N unoccupied orbitals the CCSD computation time for very large basis sets and many electrons will grow only as $n^2 N^4$, which is the same as for SD-CI. Enhancements to CCSD incorporating all excitations in a class of higher excitations (e.g. \hat{T}_3) will result in algorithms in which the time required grows as the seventh power of the size of the basis.⁽²⁰⁾

The final point to be made concerns the form of the equations for the T_2 amplitudes in Tables 2 and 3. These equations have been written in a form which emphasizes the similarity between \hat{T}_2 and $\frac{1}{2} \hat{T}_1^2$ terms. Thus, it is possible to implement terms containing \hat{T}_1^2 using subroutines already written for \hat{T}_2 terms.

IV. Implementation of the CCSD Method

At the time when we reported implementing the CCD model,⁽²⁰⁾ we briefly outlined the procedures we used for solving the nonlinear \hat{T}_2 equations. We omitted many details which we felt were self-evident; however, our subsequent experience has convinced us that a more detailed description of the algorithms should be disclosed.

First, we wish to define what we do not do. If we collect the \hat{T}_1 and \hat{T}_2 coefficients into a vector, X , and define the arrays A , B , C , D , and E , it is possible to write the equations in a general tensor form

$$A_i + \sum_j B_{ij} X_j + \sum_{ij} C_{ijk} X_{jk} + \sum_{jkl} D_{jkl} X_j X_k X_l + \sum_{jklm} E_{jklm} X_j X_k X_l X_m = 0 \quad . \quad (16)$$

In principle, equation (16) can be solved using standard approaches after constructing the matrices A , B , C , D , and E . Although we find equation (16) occasionally useful in discussing properties of the coupled cluster equations,⁽¹³⁾ the large dimension of the B , C , D , and E arrays make implementation of practically useful algorithms predicated upon the construction and manipulation of these arrays impossible. Consequently, the programs never construct these arrays; however, it is possible to think of our programs as producing the result of B , C , D , and E operating on X without explicitly constructing the arrays.

The methods used within the programs can be most simply explained by referring to the equation in Table 1 as an example. The first step is to rearrange the equation into an explicit equation for the coefficient t_ℓ^d .

Based upon our experience with perturbation theory,^(20,21) we usually choose the terms containing the diagonal Fock matrix elements (i.e., orbital energies) for the rearrangement of the T_1 equation. Thus, we would write

$$\begin{aligned}
 t_{\ell}^d = & (f_{\ell\ell} - f_{dd})^{-1} \{ f_{\ell d} + \sum_{a(\neq d)} f_{ad} t_{\ell}^a - \sum_{i(\neq \ell)} f_{il} t_i^d \\
 & + \sum_{ia} \langle di || \ell a \rangle t_i^a + \sum_{ia} f_{ia} (t_{il}^{ad} - t_{\ell}^a t_i^d) \\
 & + \dots \} .
 \end{aligned} \tag{17}$$

Equation (17) would then be solved iteratively. Usually, but not always, we start with t_{ℓ}^d initially set to 0 so that

$$t_{\ell}^d(1) = (f_{\ell\ell} - f_{dd})^{-1} f_{\ell d} \tag{18}$$

and subsequently on the j th iteration

$$\begin{aligned}
 t_{\ell}^d(j+1) = & (f_{\ell\ell} - f_{dd})^{-1} \{ f_{\ell d} + \sum_{a(\neq d)} f_{ad} t_{\ell}^a(j) \\
 & - \sum_{j(\neq \ell)} f_{il} t_i^d(j) + \sum_{ia} \langle di || \ell a \rangle t_i^a(j) \\
 & + \sum_{ia} f_{ia} (t_{il}^{ad}(j) - t_{\ell}^a(j) t_i^d(j)) + \dots \} .
 \end{aligned} \tag{19}$$

Equation (19) illustrates one additional feature of the method we use to solve the CCSD equations. Namely, we usually choose to simultaneously iterate

the equations for \hat{T}_1 and \hat{T}_2 coefficients so that at the end of the n th cycle we have all $t_{\ell}^d(n)$ and $t_{ij}^{ab}(n)$. Of course, it is possible to iterate separately for the \hat{T}_1 coefficients with frozen \hat{T}_2 coefficients and then iterate for \hat{T}_2 coefficients with fixed \hat{T}_1 . We usually find that \hat{T}_1 and \hat{T}_2 coefficients are sufficiently coupled that such an iteration method is uneconomical.

Another point which equation (19) illustrates is that we retain the nonlinearity of the CC equations throughout their solution. Usually, we do not choose to solve a linear approximation before introducing the nonlinear terms. Nor do we choose to use a Newton-Raphson method to achieve rapid convergence because the N-R method requires evaluation of a gradient matrix. The size of the gradient matrix would be too large to handle conveniently. Instead, we use a reduced linear equation method to accelerate convergence. (13)

In writing down equation (17), we choose to use the terms containing diagonal Fock matrix elements to solve for t_{ℓ}^d . This choice implies that the first few iterations of equation (17) beginning with $\hat{T}_1 = 0$ correspond to a perturbation solution of the CC equations using a Møller-Plesset partitioning of the Hamiltonian, which has been shown to normally have better convergence.⁽²²⁾ If a linear approximation to equation (17) is made, then all iterations can be made just as in perturbation theory. Although the Moller-Plesset partitioning has been shown to be superior for perturbation methods based upon Hartree-Fock orbitals, there are times when it is clearly inappropriate such as when RHF orbitals are used for an open-shell configuration and $f_{\ell\ell} = f_{dd}$. In that situation, $(f_{\ell\ell} - f_{dd})^{-1}$ is indeterminant and we have a so-called "dangerous denominator." Fortunately, in this case the dangerous denominator problem is artificial and can be eliminated by electing to add an arbitrary constant times t_{ℓ}^d to both

sides of the T_1 equation (Table 1) and then solve for t_{ℓ}^d . A simple rearrangement to other forms, like the Epstein-Nesbet partitioning for example, will not usually alleviate the denominator singularity. any circumvention does not resolve the denominator singularity. Of course, multideterminantal description implied by the dangerous denominator.

Throughout this paper, the equations have been written in spin orbital form. However, prior to implementation in the computer program, the equations are rewritten and the spin factors are specifically included. For example,

$$\begin{aligned} \sum_{\substack{a>b \\ i}} \langle i d | | a b \rangle t_{i \ell}^{ab} &\rightarrow \sum_{\substack{a_{\alpha} > b_{\alpha} \\ i_{\alpha}}} \langle i_{\alpha} d | | a_{\alpha} b_{\alpha} \rangle t_{i_{\alpha} \ell_{\alpha}}^{a_{\alpha} b_{\alpha}} \\ &+ \sum_{\substack{a_{\beta} > b_{\beta} \\ i_{\beta}}} \langle i_{\beta} d | | a_{\beta} b_{\beta} \rangle t_{i_{\beta} \ell_{\beta}}^{a_{\beta} b_{\beta}} \end{aligned} \quad (20)$$

where i_{α} refers to the spatial function of the i th spin-orbital and β orbitals are numbered higher than α orbitals. If n_{α} (n_{β}) is the number of occupied orbitals with α (β) spin and N_{α} (N_{β}) is the number of unoccupied orbitals with α (β) spin then the factoring by spin reduces the sum on the left side from $(n_{\alpha} + n_{\beta})^2$ $(N_{\alpha} + N_{\beta})^3$ to $n_{\alpha}^2 N_{\alpha}^2 (N_{\alpha} + 1)/2 + n_{\alpha} n_{\beta} N_{\alpha}^2 N_{\beta}$ operations. The equations are also analyzed to reveal simplifications which result when orbitals are spin restricted so that α and β components have the same space functions. Thus, in the spin-restricted problem $t_{\ell \alpha}^{d \alpha}$ is evaluated, but $t_{\ell \beta}^{d \beta}$ (which equals $t_{\ell \alpha}^{d \alpha}$) is not evaluated. Also terms like the second term on the right hand side of equation (20) simplify as follows in the RHF case.

$$\sum_{\substack{a \\ \beta \\ a \\ \beta \\ \alpha}} \langle i \beta | a \beta \alpha \rangle t_{i \beta \alpha}^{a b} = 2 \sum_{a_1 > b} \langle i \alpha | a b \rangle t_{i \alpha}^{a b} (1 - \delta_{ab}/2) \quad (21)$$

is

Consequently, the number of operations required drops from $n_\alpha n_\beta N_\alpha^2 N_\beta$ to $n_\alpha^2 N_\alpha^2 (N_\alpha + 1)/2$. In all cases we have been able to implement the spin-restricted sums with the same subprograms as used for the implementation of the spin-unrestricted sums by changing loop limits and inserting appropriate factors of two. As a result of explicitly treating the spin, the work involved in evaluating our equations is essentially the same as if we had adopted a spin-adapted formulation while retaining the flexibility of removing spin restrictions.

In addition to an explicit treatment of spin summations, we also factor terms containing products of three terms into intermediate partial sums containing just two terms. Thus,

$$\sum_{\substack{i > j \\ ca}} \langle i j | ca \rangle t_\ell^c t_{ij}^{da} \Rightarrow \sum_c t_\ell^c \sigma_{cd} \quad (22)$$

where $\sigma_{cd} = \sum_{\substack{i > j \\ a}} \langle i j | ca \rangle t_{ij}^{da}$. The intermediate, σ_{cd} ,

is computed and stored as partial sum before completing the evaluation by summing over the \hat{T}_1 terms. As a result of this factorization, the work required

to evaluate the above term is reduced from $n^2(n-1)N^3/2$ operations to $n^2(n-1)N^2/2 + nN^2$ operations. This is exactly the same type of simplification required to reduce the two-electron integral transformation to an $(n + N)^5$ process from an $(n + N)^8$ process; and like the explicit spin summations, it always has been used in our MBPT/CCD programs. (20-24)

Our treatment of symmetry within the program occurs at two levels and is intertwined with the choices we made for integral and coefficient storage. Hence, a brief explanation of our integral storage technique is required. Before we adopted any storage scheme we first proposed some design goals for the program:

- (1) The storage scheme adopted should facilitate writing the program. That is, it should be easier to write the required subroutines and easier to ensure the correctness of the routines.
- (2) Every step in the evaluation of the terms required should be fully factored and no term should require more than n^2N^4 , n^4N^2 or n^3N^3 operations.
- (3) Access to data, both in memory and on disk, should be sequential in the inner loops. No input/output would ever occur within the two innermost loops. Random access to records on disk would be presumed, but primarily used to position subfiles which would then be read sequentially. Because of the sequential access through memory the program would be ideally suited for virtual memory computers.

- (4) The central memory requirements, should be proportional to the square of the number of basis functions. Thus, if the computer has enough memory to solve the Hartree-Fock problem, then there should be enough memory to solve the CC problem. Unlike most CI programs, we do not assume that all of our coefficients could fit into memory. Instead, we choose to hold only a single distribution of coefficients in memory and to carefully manage the concomitant increase in input/output by working with fully ordered integrals and coefficients. Consequently, we were able to carry out frozen core CCD double zeta calculation on benzene (60 MO's) on a VAX 11-780 using a physical memory working set of 256 K bytes while paging at a relatively slow rate.(11)
- (5) Symmetry zeroes and accidental zeros should be treated transparently and on equal footing where possible.

Our approach to implementing these six goals centers on the observation that most terms in Tables 1-3 can be written as simple scalar products. For example, by combining ab, cd, and ij into single labels c, f, and k we can rewrite

$$\sum_{cd} \langle ab || cd \rangle t_{ij}^{cd} \quad (25)$$

as a simple matrix product $\sum_f V_{ef} T_{fk}$

If all $\langle ab || cd \rangle$ and t_{ij}^{ab} are sorted onto a random access device so that the label cd identifies a record containing $\langle ab || cd \rangle$ for all ab and the label ij identifies a record containing t_{ij}^{ab} for all ab, then the summation indicated in (24) is easy to perform, especially if the integrals are also ordered within each record. Furthermore, the sums can be set up so that only N^2 integrals of $\langle ab || cd \rangle$ type and N^2 coefficients of t_{ij}^{cd} type must be in memory to generate a given t_{ij}^{ab} . If integrals are ordered in each record, exact zeroes and integrals smaller than a given threshold can be removed and a skip count indicating the distance between labels can be packed into the integrals.

As a result, to simplify programming, we opt to sort the molecular orbital integrals coming out of the two-electron transformation into antisymmetrized combinations with Dirac type labels and to store them in random access subfiles according to the number and location of occupied indices. Within each subfile, two integral labels are used to specify a record containing all integrals of that type. Zero integrals and approximately zero integrals are not stored in the records and skip counts are inserted to keep track of these integrals. While these steps introduce some inefficiency and redundancy at the N^4 level, we are willing to make these kinds of sacrifices to speed up the N^6 processes.

Returning to the treatment of symmetry, we see that at the lowest level symmetry is implemented by removing all zeroes from the antisymmetrized integral and coefficient lists. While it is important to remove zeroes for integral and coefficient storage, the principal benefit occurs during the construction of the scalar products where a routine like that shown in Table 4 can be used to perform a sparse scalar product. Thus, the inner most loops are implemented with a sparse scalar product subroutine which is driven by the indices implicit within the antisymmetrized integral list. Since indices which are zero by symmetry never appear, the loops effectively run only over symmetry indices. To avoid generating a term which is zero by symmetry, we use a symmetry template in the outermost loops. Thus, the target arrays contain a bit flag which indicates whether the sum is zero by symmetry. In effect, the outermost loops run over all orbital indices, but the inner loops are skipped altogether if the evaluation term must be zero by symmetry.

This completes the discussion of the computational considerations. The following section discusses some applications of the CCSD model to molecules.

VI. EXAMPLES

Our first application of the CCSD model was to H_2 in a double zeta basis. A potential curve from 0.9 a.u. through 10 a.u. was calculated with both the CCSD model and SDCI (i.e. full CI), which of course, gave the same answer. Furthermore, the CCSD energy was invariant to the orbital transformations - including UHF orbitals- which we applied to test the program.

The second application, also made to test the correctness of the program, was $2H_2$ at a 100 a.u. intermolecular separation. In this problem, the CCSD energy was exactly twice the SDCI energy for a single H_2 as size extensivity requires. Again, the correct relationship held for the range of H_2 intramolecular separations while keeping the intermolecular separation of the H_2 's at 100 a.u.

More interesting results are the CCSD energies for H_2O and the comparison with the full CI results of Saxe, Schaefer and Handy (Table 5).⁽²⁴⁾ Our CCSD energy, in the double zeta basis at their geometry, is -76.156077 hartrees which represents an energy lowering of -.006062 hartrees relative to their SD-CI energy of -76.150015 hartrees. Our CCSD energy is .001789 hartrees above their full CI energy of -76.157866 hartrees. The largest part of the difference between CCSD and full CI comes from triple excitations, which have been calculated to contribute -0.001364 hartrees.⁽²⁵⁾ The CCSD energy accounts for 98.79% of the total correlation energy compared to 94.67% for SD-CI. Thus, the CCSD model accounts for two-thirds of the error inherent in SD-CI. As can be seen from Table 5, the CCSD + T(4) model energy is .00017 hartrees (0.1 kcal/mole) above the SDTQ-CI energy. In this case, the effect of CI type quadruple excitations are handled accurately by the exponential ansatz.

Equally interesting is a comparison of CCSD with CCSD-2, a simplification of the full CCSD in which only the linear single excitation terms and the $1/2T_1^2$ are retained.⁽¹³⁾ The difference between CCSD and CCSD-2 of .00031 hartrees is the energy raising caused by disconnected single contributions to CI type triple and quadruple excitations.

One of the advantages of an infinite-order model like CCSD over a finite-order perturbation approximation occurs with more difficult cases that involve some quasidegeneracy.⁽²⁰⁾ Unlike the H_2O example, where the Hartree-Fock reference determinant has a coefficient of 0.95 in the full CI expansion with all other coefficients very small, a quasidegenerate problem usually has two or more configurations with comparatively large coefficients, which might recommend a multireference approach. However, the infinite-order CCD model relative to only a single reference function has been shown to often describe even highly degenerate problems reliably.⁽¹²⁾ Consequently, to assess the stability of the CCSD model for quasidegenerate cases, a problem involving the insertion of Be into an H_2 molecule has been considered.

Be is well-known for the quasidegeneracy between the 2s and 2p orbital that causes the $1s^2 2p^2$ configuration to be important in the CI expansion. The degree of importance of the $1s^2 2p^2$ configuration is very much a function of the choice of molecular orbitals with MCSCF orbitals weighting it heavily, but even with SCF orbitals from a large basis set, the coefficient is still about 0.1.⁽²⁰⁾ Also, as the H_2 bond is broken, the $1\sigma_g^2$ and $1\sigma_u^2$ configurations become equally important. In addition, to these elements, as Be is inserted perpendicularly (C_{2v}) into H_2 , there is

a promotion from $\text{Be}(2s^2)$ to $\text{Be}(2p^2)$ near the critical geometry, causing the principal configuration for BeH_2 to change from $1a_1^2 2a_1^2 3a_1^2$ to $1a_1^2 2a_1^2 1b_2^2$. Since in a single reference model, one of these configurations must be treated in the complementary space, such quasidegeneracy effects should severely tax the ability of a single reference model to describe this insertion reaction. Also, both RHF functions are unstable since a lower UHF solution exists. Just as in full CI, however, even a poor choice of single reference function might be used to generate the configurations, but the proper weight factors would be obtained via the diagonalization step. CCSD potentially has the same flexibility, although one must distinguish between a method containing the correct solution and the practical problem of extracting that solution numerically. In all applications reported here the reduced linear equation method and Padé approximants⁽¹³⁾ are used to obtain the solutions.

The basis set for BeH_2 is given in Table 6, and we present the SCF, full CI, CCSD and various lower order MBPT results in Table 7. The geometry, $\text{Be}(0., 0., 3.0 \text{ a.u.})$ and $\text{H}(0. \pm 1.16 \text{ a.u.}, 0.)$, is near the point of crossover when the principal configuration $1a_1^2 2a_1^2 3a_1^2$ would be superseded by $1a_1^2 2a_1^2 1b_2^2$. The full CI coefficients using SCF orbitals obtained from $1a_1^2 2a_1^2 1b_2^2$ at this geometry are 0.823 and -.294, respectively. When Be is moved to 2.75 a.u. from H_2 , the respective coefficients change to -.560 and 0.724.

Despite the large amount of potential degeneracy in this system the agreement between the single reference CCSD model and the full CI is exceptional. Unlike the example of H_2O where fourth-order perturbation theory (SDTO-MBPT(4)) is only 0.6 kcal/mole higher than the full CI, and

the other fourth-order approximations are in the vicinity of 2 kcal/mole of the full CI, the error is 6-7 kcal/mole for fourth-order approximations for BeH_2 .

An even more extreme test example is to choose to use the less important $1a_1^2 2a_1^2 1b_2^2$ configuration as the reference determinant. Its coefficient of 0.294 corresponds to a weight of less than 10% of the full CI wavefunction. These results are listed in Table 8. Notice that the SCF result is much higher and, in fact, seems to be approximating the second root of the full CI. The perturbation approximations tend to cluster in the vicinity of the second eigenvalue although they do go below the correct answer, assuming some kind of average value between the two eigenvalues. However, the CCSD model appears to overcome the comparatively poor starting point to a large degree, getting within 5.3 kcal/mole of the full CI. This occurs despite the enormous weight of the $1a_1^2 2a_1^2 3a_1^2$ configuration (2.16 intermediately normalized) in the CCSD wavefunction. BeH_2 has an approximately separated pair structure and the basis set is small, but this example still illustrates the large degree of flexibility inherent in the CCSD model. Combining CCSD's stability, with its efficiency, size-extensivity, and its equivalence to the full CI for the chemically pertinent problem of a group of separated electron pairs, appears to make CCSD a very attractive model for numerous applications.

APPENDIX A

APPENDIX A

The CI Eigenvalue Problem in Energy Independent Form

Consider the problem of finding an eigenvalue satisfying

$$(\underline{H} - E \underline{\xi}) \underline{\xi} = 0 \quad (A-1)$$

where \underline{H} is a symmetric matrix and $\underline{\xi}$ is the eigenvector corresponding to the energy eigenvalue E . One technique for solving secular equations is the partitioning method. Here we partition equation (A-1) and renormalize it so that

$$\begin{bmatrix} \underline{H}_0 - E \underline{\xi} & \underline{a} \\ \underline{a}^+ & \underline{B} - E \underline{\xi} \end{bmatrix} \begin{bmatrix} 1 \\ \underline{t} \end{bmatrix} = 0 \quad (A-2)$$

which is equivalent to two equations

$$\underline{H}_0 - E \underline{\xi} + \underline{a} \underline{t} = 0 \quad (A-3)$$

and

$$\underline{a}^+ + (\underline{B} - E \underline{\xi}) \underline{t} = 0 \quad (A-4)$$

Solving (A-3) for E we find

$$E = \underline{H}_0 + \underline{a} \underline{t} \quad (A-5)$$

which we use in (A-4) to get

$$\underline{a} + (B - H_C \underline{1}) \underline{t} = (\underline{a} \underline{t}_1) \underline{t} = 0 \quad . \quad (A-6)$$

Equation (A-6) is independent of E and equivalent to equation (A-2).

The energy corresponding to the \underline{t} which satisfies (A-6) is given by (A-5). The quadratic dependence manifest in (A-6) is different from that present in the coupled cluster equation, since in (A-6) there is a scalar product, while in the coupled cluster equations a true tensor product, $\underline{t} \times \underline{t}$, appears.

Equation (A-6) also has an additional interesting feature in that the linearized coupled cluster method can be derived by deleting $-(\underline{a} \underline{t}_1) \underline{t}$ from (A-6).

Table 1. CCSD equation satisfied by single excitation coupled cluster coefficients t_{ℓ}^d

$$\begin{aligned}
 & f_{\ell d} + \sum_a f_{ad} t_{\ell}^a - \sum_i f_{il} t_i^d + \sum_{ia} \langle di || \ell a \rangle t_i^a + \sum_{ia} (t_{il}^{ad} - t_{\ell}^a t_i^d) f_{ia} \\
 & + \sum_{\substack{a>b \\ i}} \langle id || ab \rangle (t_{il}^{ab} + t_i^a t_{\ell}^b - t_{\ell}^a t_i^b) - \sum_{\substack{i>j \\ a}} \langle ij || al \rangle (t_{ij}^{ad} + t_i^a t_j^d - t_j^a t_i^d) \\
 & - \sum_{\substack{i>j \\ ca}} \langle ij || ca \rangle t_{\ell}^c t_{ij}^{da} - \sum_{\substack{ik \\ a>b}} \langle ik || ab \rangle t_k^d t_{il}^{ab} \\
 & - \sum_{\substack{kc \\ jb}} \langle jk || cb \rangle t_k^c (t_{\ell j}^{db} - t_{j\ell}^d t_{\ell}^b) = 0
 \end{aligned}$$

TABLE 2. CCSD equation satisfied by the double excitation coefficient t_{ij}^{ab}

$$\begin{aligned}
 & \langle ij || ab \rangle - \sum_d [f_{bd} c_{ij}^{ad} + f_{ad} c_{ij}^{db}] + \sum_k [f_{kj} c_{ik}^{ab} + f_{ki} c_{kj}^{ab}] \\
 & + \sum_k [\langle ak || ij \rangle t_k^b + \langle kb || ij \rangle t_k^a] - \sum_c [\langle ab || cj \rangle t_i^c + \langle ab || ic \rangle t_j^c] \\
 & + \sum_{c>d} \langle ab || cd \rangle c_{ij}^{cd} + \sum_{k>l} \langle ij || kl \rangle c_{kl}^{ab} \\
 & - \sum_{k,d} [\langle bk || jd \rangle \tilde{c}_{ki}^{ad} - \langle bk || id \rangle \tilde{c}_{kj}^{ad} - \langle ak || jd \rangle \tilde{c}_{ik}^{db} + \langle ak || id \rangle \tilde{c}_{jk}^{db}] \\
 & - t_k^a t_{ij}^{cb} - t_k^b t_{ij}^{ac} - t_i^c t_{kj}^{ab} - t_j^c t_{ik}^{ab} \\
 & + \sum_d [\eta_{ij}^{bd} t_{ij}^{ad} - \eta_{ij}^{ad} t_{ij}^{bd}] - \sum_\ell [\eta_{\ell j}^{ab} t_{i\ell}^{ab} - \eta_{\ell i}^{ab} t_{j\ell}^{ab}] \\
 & + \sum_c [t_i^c \alpha_{ab; cj} - t_j^c \alpha_{ab; ci}] + \sum_\ell [t_\ell^a \alpha_{ij; \ell b} - t_\ell^b \alpha_{ij; \ell a}] \\
 & + \frac{1}{4} \sum_{\substack{k \ell \\ c d}} \langle kl || cd \rangle [c_{ij}^{cd} c_{kl}^{ab} - 2(t_{ij}^{ac} c_{kl}^{bd} + t_{ij}^{bd} c_{kl}^{ac}) \\
 & - 2(t_{ik}^{ab} c_{jl}^{cd} + t_{jl}^{bd} c_{ik}^{cd}) + 4(\tilde{c}_{ki}^{ac} \tilde{c}_{lj}^{bd} + \tilde{c}_{ki}^{bd} \tilde{c}_{lj}^{ac})] \\
 & - 8 t_i^d t_k^b t_\ell^a t_j^c = 0
 \end{aligned}$$

TABLE 3. DEFINITIONS OF QUANTITIES IN TABLE 2

$$A_{ij}^{ab} \equiv t_{ij}^a t_j^b - t_{ji}^a t_i^b$$

$$C_{ij}^{ab} \equiv t_{ij}^{ab} + A_{ij}^{ab}$$

$$\tilde{C}_{ij}^{ab} \equiv t_{ij}^{ab} + t_i^a t_j^b$$

$$B_{ij}^{ab} \equiv t_{ij}^{ab} + A_{ij}^{ab}/3$$

$$\tilde{B}_{ij}^{ab} \equiv t_{ij}^{ab} + t_i^a t_j^b/3$$

$$\eta^{bd} \equiv \sum_{kc} \langle bk || dc \rangle t_k^c$$

$$\eta_{\ell j} \equiv \sum_{kc} \langle k\ell || cj \rangle t_k^c$$

$$\alpha_{ab;cj} \equiv \sum_{kd} \langle bk || cd \rangle \tilde{B}_{kj}^{ad} - \sum_{kd} \langle ak || cd \rangle \tilde{B}_{kj}^{bd} + \sum_{k>\ell} \langle \ell k || jc \rangle B_{k\ell}^{ab}$$

$$\alpha_{ij;\ell b} \equiv \sum_{kc} \langle \ell k || cj \rangle \tilde{B}_{ik}^{cb} - \sum_{kc} \langle \ell k || ci \rangle \tilde{B}_{jk}^{cb} + \sum_{c>d} \langle bl || cd \rangle B_{ij}^{cd}$$

TABLE 4. A FORTRAN SUBROUTINE FOR PERFORMING
A SPARSE SCALAR PRODUCT
FUNCTION PAKPRD (A, LA, B, LB, N)

```
C
C PAKPRD PERFORMS A PACKED SCALAR PRODUCT
C BETWEEN VECTOR A AND VECTOR B
C
C A : AN ARRAY OF NUMBERS WITH SKIP INDICES
C LA : THE LENGTH OF A
C B : AN ARRAY OF NUMBERS WITH SKIP INDICES
C LB : THE LENGTH OF B
C N : THE LENGTH OF A AND B IF THEY WERE UNPACKED
C

PAKPRD = 0.
IA = 0
IB = 0
NA = 0
NB = 0
40 IA = IA + 1
    NA = NA + (A(IA) .AND. 225)
30 IB = IB + 1
    NB = NB + (B(IB) .AND. 255)
50 IF (NA-NB) 10, 20, 30
20 PAKPRD = PAKPRD + A (IA)*B(IB)
    IF (NA .LT. N) GO TO 40
    IF (NB .GT. N) CALL BOMB (NB)
    IF (IB .GT. LB) CALL BOMB (IB)
    IF (IA .GT. LA) CALL BOMB (IA)
    RETURN
10 IA = IA + 1
    NA = NA + (A(IA) .AND. 255)
    GO TO 50
END
```

TABLE 5. COMPARISON OF MBPT/CCM RESULTS WITH FULL CI
 H_2O IN 14 CGTO BASIS SET FROM SAXE, SCHAEFER
 AND HANDY^a

Model	Configurations	Correlation Energy	$\Delta E(FCI)$ Kcal/mole
SD-CI	361	-0.14018	4.9
SDTQ-CI	17,678	-0.14777	0.2
FULL CI	256,743	-0.14803	0.0
D-MBPT(2)		-0.13948	5.4
D-MBPT(3)		-0.14087	4.5
D-MBPT(4)		-0.14392	2.6
DQ-MBPT(4)		-0.14476	2.1
SDQ-MBPT(4)		-0.14565	1.5
SDTQ-MBPT(4) ^b		-0.14704	0.6
CCD		-0.14544	1.6
CCD-Orbital Optimized		-0.14622	1.3
CCD + ST(4)		-0.14771	0.2
CCSD-1 or 2		-0.14655	0.9
CCSD		-0.14624	1.2
CCSD + T(4)		-0.14760	0.3

^a Reference (24).

^b Reference (25).

TABLE 6. CONTRACTED GAUSSIAN BASIS USED FOR THE TEN
ORBITAL BeH_2 MODEL PROBLEM

		<u>Exponent</u>	<u>Contraction Coefficient</u>
Be	1s	1267.07	.001940
		190.356	.014786
		43.2959	.071795
		12.1442	.236348
		3.80923	.471763
		1.26847	.355183
	1s'	5.693880	-0.028876
		1.555630	-0.177565
		0.171855	1.071630
	1s''	0.057181	1.000
	2p	5.693880	.004836
		1.555630	.144045
		0.171855	.949692
H	1s	19.2406	.032828
		2.8992	.231208
		0.6534	.817238
	1s'	0.17760	1.000

TABLE 7. COMPARISON OF BeH_2 ENERGIES CALCULATED NEAR THE
 TRANSITION STATE GEOMETRY $\text{BE}(0., 0., 3. \text{ a.u.})$
 $\text{H}(0., +1.16 \text{ a.u.}, 0.)$ REFERENCE CONFIGURATION $a_1^2 a_1^2 a_1^2$ *

Model	Configurations	Total Energy	$\Delta E(\text{FCI})$ kcal/mole
SCF	1	-15.53647	55.5
FCI	1574	-15.62496	0.0
D-MBPT(2)		-15.58485	25.2
D-MBPT(3)		-15.60460	12.8
D-MBPT(4)		-15.61437	6.6
SD-MBPT(4)		-15.61485	6.3
DQ-MBPT(4)		-15.61331	7.3
SDQ-MBPT(4)		-15.61378	7.0
CCSD-2		-15.62709	1.3
CCSD		-15.62418	0.5

* CCSD expansion coefficient for $a_1^2 a_1^2 b_2^2 = -0.24$
 using intermediate normalization.

TABLE 8. COMPARISON OF BeH_2 ENERGIES CALCULATED AT
 $\text{Be} (0., 0.3 \text{a.u.}) \text{H} (0., \pm 1.16 \text{a.u.}, 0.)$ WITH
 REFERENCE CONFIGURATION $a_1^2 a_1^2 b_2^2$ *

Model	Configurations	Total Energy	$\Delta E(\text{FCI})$ kcal/mole
SCF	1	-15.47728	92.7
FCI Root 1	1574	-15.62496	0.0
FCI Root 2	1574	-15.53575	56.0
D-MBPT(2)		-15.51987	65.9
D-MBPT(3)		-15.53564	56.0
D-MBPT(4)		-15.54422	50.7
SD-MBPT(4)		-15.54495	50.2
DQ-MBPT(4)		-15.54331	51.2
SDQ-MBPT(4)		-15.54404	50.8
CCSD		-15.61645	5.3

* CCSD expansion coefficient for $a_1^2 a_1^2 a_1^2 = 2.16$
 using intermediate normalization.

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